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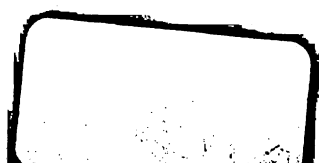
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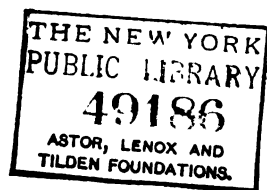
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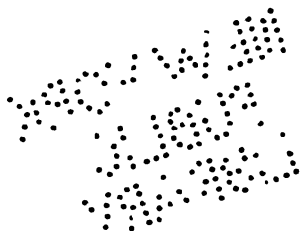
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NEW COMBINATION OF ARGON: SYNTHESIS AND ANALYSIS.

By M. BERTHELOT.

THE knowledge of the action of carbon disulphide upon nitrogen when submitted to the electric effluve led me to try the same influence upon argon. The experiment has been fully successful; it gives rise to a combination more rapid and complete than that produced with benzene, and not apparently limited like that of phenomena of equilibrium. In each case the mercury intervenes chemically, as I have recognised in my recent experiments.

I operated upon 6.55 c.c. of argon, as pure as possible, and such that benzene, employed once, did not determine (under the influence of the effluve) a direct absorption exceeding nine-hundredths. I brought the gas into contact with liquid carbon disulphide at about 20°, a temperature at which the tension of the sulphide rises to 0.98 metre. This fact has been taken account of.

After three hours of the effluve, under the conditions described in case of nitrogen, the absorption of the argon rose to 11 per cent of its initial volume. After eight hours it increased to 17 per cent.

The gases of the recipient were changed, and a new dose of carbon disulphide was added.

A third reaction of the effluve raised the absorption to 22 per cent; a fourth reaction to 34 per cent; and a fifth reaction to 39 per cent.

The gases of the recipient were changed again; a further dose of carbon disulphide was added, and the experiment was resumed. The total absorption increased then to 56 per cent. The argon represented only 2.9 c.c. An accident prevented me from prolonging this experiment, which had lasted about sixty hours.

But it is scarcely doubtful but that it would have ended in total absorption. It did not appear limited by an inverse reaction, and it is not accompanied at the ordinary pressure by a fluorescence visible in full daylight, and capable of giving rise in diffused light to special spectroscopic rays.

These characters distinguish the absorption of argon by carbon disulphide from its absorption by benzene. In fact, the latter is slower, and is limited by reactions of dissociation which stop the direct action, effected once, at about 9 or 10 per cent with pure argon. Indeed, on separating the unabsorbed argon from its products, we may renew the action, but always with difficulty. After sixty hours, with

renewal, I have not gone beyond 16 per cent. Lastly, the absorption of argon by benzene determines the formation of a fluorescent vapour, giving at atmospheric pressure a fine green, visible in full daylight, in which we distinguish among others the rays of the vapour of mercury, *i.e.*, the indication of the presence of a volatile compound of mercury formed in the reaction of argon with the hydrogen carbide. On the contrary, no fluorescence of this kind at this pressure is observed during the absorption of argon by carbon disulphide.

I shall soon return anew to the study of this extraordinary fluorescence. But at present I may mention that it constitutes an essential difference between the combination of argon with the elements of carbon disulphide and its combination with the elements of benzene. Nitrogen gives nothing analogous.

I submitted the product of the reaction to a special examination. The compound naturally contains mercury, but we cannot decide whether this element is associated with argon in one and the same compound. If treated with sodium sulphide it does not give reactions analogous to those of sulphocyanide, except a slight yellow colouration (after acidification) with ferric salts.

I have succeeded in regenerating argon from the compound just mentioned. In this new research I avoided taking the product which had absorbed the first doses of the gas, as it might contain nitrogen if any remained in the argon used for the experiment.

I operated upon the second product, which had absorbed 1.2 c.c. of argon; I submitted this product at once to the action of heat, in the same tubes in which it had been condensed over the mercury after the complete evacuation of the gases, and operating as it had been done in case of carbon disulphide.

Whilst this operation performed on the product of the absorption of nitrogen by carbon disulphide yielded only an insignificant residue, with the product of argon I obtained 0.62 c.c., *i.e.*, equal to about half the volume of the gas absorbed. This number, however, is too low, considering that a very considerable part of the condensed product escapes the action of heat, because of the impossibility of causing the mercury to boil as far as the lower and expanded part of the test-tubes, whereby a portion of the transformed matter is deposited. The contracted part alone is raised to about 500°. Thus the figures given have a merely qualitative meaning, being intended to give some idea of the order of greatness of the phenomena.

I will add that I have caused the condensed product, in

the annular intervals of the two tubes, to undergo three successive heatings to dull redness, evacuating each time the gases produced and collecting them again separately. Their gross volume amounted to several c.c. by reason of the regeneration of the carbon disulphide, a circumstance which ensures the most complete elimination of the other gases.

The first heating yielded, after the reaction of the alcoholised potassa and acid cuprous chloride, and final purification by potassa, volume = 0.41 c.c.; the second heating, 0.20 c.c.; the third heating, 0.01 c.c.

The decomposition of heat is thus exhausted in the portion of the substance capable of being heated to dull redness.

To verify if the gas thus regenerated is really argon, I had recourse to the only positive character obtainable in my apparatus, i.e., the production of the fluorescent spectrum developed by benzene at the ordinary pressure. I used effluve-tubes of reduced dimensions, such that 0.40 c.c. of the regenerated gas occupied in the first place a length of 5 or 6 cm. By operating thus I succeeded, in fact, in obtaining most distinctly, at a pressure bordering upon that of the atmosphere, the green fluorescence characteristic of the compound of argon and benzene. The 0.40 c.c. were reduced thus in eight hours to 0.35 c.c., the absorption taking place with the slowness characteristic of argon, and reaching the same limit. I repeated the same test with 0.12 c.c. of the gas regenerated by the second heating with the same success, and I established in both cases the existence of the specific rays of this fluorescence, developed in diffused light and near the normal pressure.

This experiment seems to me capital, since it demonstrates that argon can enter into combination and be regenerated with its original properties.—*Comptes Rendus*, cxx., p. 1316.

PREPARATION AND PROPERTIES OF PURE MELTED MOLYBDENUM.

By HENRI MOISSAN.

In a former paper we have shown that it is easy to produce cast molybdenum, by heating in the electric furnace a mixture of charcoal and of the oxides of this metal. We shall now give the continuation of our researches on this question.

We must first mention that molybdenum, which is obtained in a pulverulent state by the reduction of the binoxide in hydrogen, was fused by Debray before the blowpipe only in the form of small globules containing 4 to 5 per cent of carbon.

To prepare molybdenum we set out from pure ammonium molybdate, reduced to powder and placed in a crucible of refractory earth, No. 12, capable of containing 1 kilo. The crucible, covered with its lid, is heated for one and a half hours in a Perrot furnace. After cooling, the oxide is a dense powder of a violet-grey, corresponding to the formula MoO_3 . One heating yields from 760 to 770 grms. of oxide. This oxide was mixed with sugar-charcoal, in powder, in the following proportions:—

Oxide	300 grms.
Charcoal	30 "

In this mixture the oxide is in decided excess compared with the charcoal. The powder is heaped up in a crucible of coke and submitted to the action of an arc produced by a current of 800 ampères and 60 volts for six minutes. We must avoid the complete fusion of the metal, so as to leave a solid layer in contact with the crucible which would be strongly attacked by the liquid molybdenum. Under these conditions we obtain a metal perfectly pure and free from carbon; it is easy in one hour to prepare more than 1 kilo.

If this preparation lasts more than six minutes, the molybdenum obtained is liquefied, corrodes the crucible, becomes carburetted, and we obtain a grey cast metal, very hard and brittle.

Cast Molybdenum.

This cast metal has a specific gravity of 8.6 to 8.9, according to its proportion of carbon. When saturated with carbon it is much more fusible than molybdenum. When rich in carbon it is grey and brittle; at 12.5 per cent of carbon it becomes white, and can be broken up upon the anvil only with difficulty. It presents all the characteristics of the molybdenum studied by Debray. It rapidly dissolves carbon, and abandons it on cooling in the state of graphite, precisely as does cast-iron. Nevertheless, when saturated with carbon it yields a carbide, crystallised in fine needles. Grey cast-molybdenum is very hard; it scratches steel and quartz. When melted, it becomes a very mobile liquid, which can be poured whilst giving bright sparks and abundant fumes of molybdic acid. We have been able to melt and cast ingots of from 8 to 10 kilos. These castings had the following compositions:—

	White.	Grey.
Molybdenum	95.83	92.46
Combined carbon ..	3.04, 3.19, 2.54	4.90, 5.50
Graphite	0.00	0.00, 1.71
Slags	0.74, 0.53, 0.62	—

Molybdenum Carbide.

This compound is prepared by heating in the electric furnace molybdenum binoxide with an excess of charcoal. The best proportions are:—Binoxide, 250 grms.; charcoal, 50 grms. The duration of the heating is from eight to ten minutes with a current of 800 ampères and 50 volts. If we use an excess of charcoal it is found in the mass in the state of graphite.

The regulus obtained is of a brilliant white and has a crystalline fracture; it splits readily. It is readily crushed on the anvil, and we may separate from it small elongated prisms of a distinct crystallisation. Its specific gravity is 8.9, and its composition is Mo_2C .

Analysis.

In the various specimens described in this memoir, the molybdenum, after treatment with nitric acid, has been precipitated as mercurous molybdate, and finally determined as bioxide. When the carbide contains no graphite, the carbon was separated by pure dry chlorine, and then determined by combustion in oxygen, according to the weight of carbonic acid collected. According to this method, the portions of carbon are always rather low.

We have obtained the following figures:—

				Theory for Mo_2C .
Molybdenum	93.82	—	—	94.12
Combined carbon ..	5.62	5.53	5.48	5.88
Graphite	—	—	—	—
Slags	0.17	—	—	—
	99.61			

If the carbide contains graphite it is attacked in a flat-bottomed flask traversed by a current of oxygen. The gases evolved pass into a tube filled with copper oxide, the watery vapour is retained in a tube filled with sulphated pumice, and the carbonic acid is fixed in potassa. The increase of the weight of the potassa tube shows the carbonic acid, and consequently, the carbon. The acid liquid of the flask, after filtration and washing, shows the graphite, and the molybdenum is next determined by mercurous nitrate. This novel method gave as results:—

	9.	10.
Molybdenum	92.60	91.90
Combined carbon ..	5.15	5.43
Graphite	1.61	1.98

On taking account of the graphite and calculating the proportion of molybdenum to the carbon we find:—

	9.	10.	Theory Mo ₂ C.
Molybdenum	94.45	94.10	94.12
Combined carbon	5.55	5.90	5.88

Pure Fused Molybdenum.

Pure molybdenum has a specific gravity of 9.01. It is a metal as malleable as iron. It can be easily filed and polished, and forged hot. It does not scratch either quartz or glass. When free from carbon and silicon, it scarcely oxidises in the air below a dull redness. It may be kept for several days unchanged in water, whether ordinary or charged with carbonic acid. In presence of air below dull redness it is covered with an iridescent film, as is steel. About 600° it begins to be oxidised, and yields molybdic acid, which is slowly volatilised.

A fragment of molybdenum heated for some hours in a sloping porcelain tube over an analytical furnace yields, in the upper part of the tube, a felted mass of crystals of molybdic acid. The metal is not covered with any other oxide, and finally disappears, leaving a fine crystallisation of molybdic acid. If heated before the gas-blowpipe, a fragment of molybdenum emits vapours in considerable quantity. If heated before the oxyhydrogen blowpipe, it burns without melting, giving off abundant fumes of molybdic acid and leaving a blue oxide, sparingly fusible. If heated in a current of pure oxygen, it takes fire between 500° and 600°; and if the current is rapid the combustion may continue without the intervention of any extraneous source of heat.

This combustion ensues with intense incandescence, and may serve as a fine lecture experiment.

Melting potassium chlorate attacks molybdenum with violence. The chlorate is melted, and a fragment of molybdenum thrown upon its surface, when it becomes incandescent and revolves upon the surface of the liquid.

The temperature of the reaction rises rapidly, the molybdenum burns with flame, and there escape abundant white fumes of molybdic acid, which remain suspended in the air in the form of white floating filaments. Sometimes the fragment of molybdenum is raised to a temperature high enough to perforate the side of the capsule, which is melted in contact with the metal.

Melting potassium nitrate under similar conditions yields a reaction similar, though less violent, with formation of an alkaline molybdate.

A mixture of molybdenum and lead peroxide heated in a test-tube produces a great liberation of heat and light.

Sulphur has no action at 440°, but hydrogen sulphide at 1200° transforms molybdenum into a bluish grey sulphide, amorphous, having the properties of molybdenite, and leaving, on friction, a black mark upon paper.

Fluorine does not attack molybdenum in fragments, but if the metal is coarsely powdered, there is formed, without incandescence, a volatile fluoride.

Chlorine attacks molybdenum at dull redness, but without incandescence. With bromine, the action takes place at a cherry-red heat, but without great intensity.

Iodine has no action at the temperature of softening glass.

Silver, zinc, and lead fluorides are decomposed, but without the formation of volatile fluorides.

Phosphorus perchloride, if slightly heated, readily attacks molybdenum, forming a volatile chloride, which is easily modified in presence of atmospheric moisture, taking a fine blue colouration.

This reaction is produced with most of the compounds of metallic molybdenum—the oxides, the sulphide, molybdic acid, and the molybdates. It may serve for the rapid detection of metallic molybdenum or its compounds. It is effected in the following manner:—

Into a small test-tube we put a fragment of the substance in question, adding a little phosphorus perchloride, and heating gently. There are formed reddish fumes of molybdenum chloride and oxychloride which condense in

a brown ring more or less intense. If the quantity of molybdenum is very slight, the ring may be scarcely visible. It will then be sufficient to expose it to moisture to see it take an intense blue tint, due to the formation of hydrated chloride.

The action of hydracids upon pure molybdenum is almost similar to that which they exert upon cast molybdenum. These experiments, however, have been described by different observers, Bucholz, Berzelius, and Debray. We merely mention that hydrofluoric acid does not attack it, but on adding a drop of nitric acid the action sets in and continues with energy. In presence of a mixture of equal parts of the two acids the solution is complete, and there remains a rose-coloured liquid which, with ferrocyanide, gives an intense red-brown colour, but no precipitate. The mass some hours afterwards coagulates to a jelly.

In a current of nitrogen at 1200°, molybdenum, whether in fragments or in powder, does not form a nitride.

It does not combine with phosphorus at the temperature of melting glass.

Boron combines with molybdenum at the temperature of the electric furnace, yielding an iron-grey melted mass containing cavities lined with prismatic needles.

Under the same conditions, silicon yields a crystalline silicide not fusible before the oxyhydrogen blowpipe.

The action of carbon deserves to arrest our attention for a few moments.

Pure molybdenum, as above described, is a soft metal, which is easily filed and which does not even scratch glass. If we heat a fragment of molybdenum for some hours to a temperature close on 1500° in the midst of a mass of charcoal in powder, it becomes cemented, takes up a small quantity of carbon, and its hardness increases so that it can scratch glass. If we then heat it to 300° and plunge it suddenly into cold water, it is tempered, becomes brittle, and hard enough to scratch rock crystal.

Inversely, if we take cast molybdenum containing 4 per cent of carbon, very hard and brittle, and heat a fragment for some hours with molybdenum binoxide in a lined crucible, it becomes refined, and its surface may then be readily filed and polished.

I attribute this decarburation of the solid cast molybdenum at a temperature very remote from its melting-point to the ready diffusion of vapours of molybdic acid through the metal. I consider that these properties may find applications in metallurgy.

If, in a metal saturated with oxygen, such as is obtained in the first period in the Bessemer converter, we wish to remove this oxygen, we add manganese, which is oxidised more easily than iron, and then passes into the slag (Troost and Hautefeuille). It has been also proposed to employ aluminium, which has given good results, because it is combustible, *i.e.*, because it seizes on the oxygen, but which has the inconvenience of producing solid alumina. I think that molybdenum may be used under the same conditions; it would have the advantage—

1. Of yielding a volatile oxide, molybdic acid, which would be liberated immediately in the gaseous state, stirring up the whole mass.

2. Used in a slight excess it would leave in the bath a metal as malleable as iron, and capable of being tempered along with the latter.

The powder of molybdenum, which it has been attempted to use already, cannot render the same services, because it burns rapidly upon the surface of the bath in contact with the air without having yielded any useful effect.

Analysis of Pure Molybdenum.

	11.	12.	13.	14.
Molybdenum ..	99.98	99.37	99.89	99.78
Carbon	0.00	0.01	0.00	0.00
Slag	0.13	0.28	0.08	0.17

—Comptes Rendus, cxx., p. 1320.

ON THE
NEW GAS OBTAINED FROM URANINITE.*
(FIFTH NOTE).

By J. NORMAN LOCKYER, C.B., F.R.S.

IN a former communication I pointed out the spectroscopic evidence, furnished by the isolation of lines in certain minerals, which indicates that the complete spectrum obtained when bröggerite is submitted to the distillation method is produced by a mixture of gases.

In order to test this view, I have recently made some observations, based on the following considerations:—

1. In a simple gas like hydrogen, when the tension of the electric current given by an induction coil is increased, by inserting first a jar, and then an air-break into the circuit, the effect is to increase the brilliancy and the breadth of all the lines, the brilliancy and breadth being greatest when the longest air-break is used.

2. Contrariwise, when we are dealing with a known compound gas; at the lowest tension we may get the complete spectrum of the compound without any trace of its constituents, and we may then, by increasing the tension, gradually bring in the lines of the constituents, until, when complete dissociation is finally reached, the spectrum of the compound itself disappears.

The unequal behaviour of the lines has been further noted in another experiment, in which the products of distillation of bröggerite were observed in a vacuum tube and photographed at various stages. After the first heating, D_3 and 4471 were seen bright, before any lines other than those of carbon and hydrogen made their appearance. With continued heating, 667, 5016, and 492 also appeared, although there was no notable increase of brightness in the yellow line; still further heating introduced additional lines 5048 and 6347.

These changes are represented graphically in the following diagram (fig. 2):—

It was recorded further that the yellow line was at times dimmed, while the other lines were brightened.

In my second note communicated to the Royal Society on the 8th instant, I stated that I had never once seen the lines recorded by Thalén in the blue, at λ 4922 and 4715.

It now seems possible that their absence from my previous tubes was due to the fact that the heating of the minerals was not sufficiently prolonged to bring out the gases producing these lines.

It is perhaps to the similar high complexity of the gas obtained from clèveite that the curious behaviour of a tube which Professor Ramsay was so good as to send me must be ascribed. When I received it from him, the

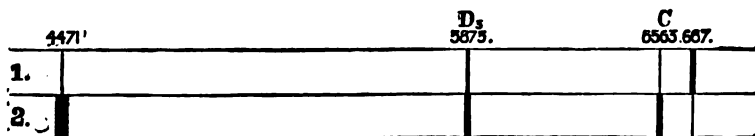


FIG. 1.
Diagram showing changes in intensities of lines brought about by varying the tension of the spark. 1. Without air-break. 2. With air-break.

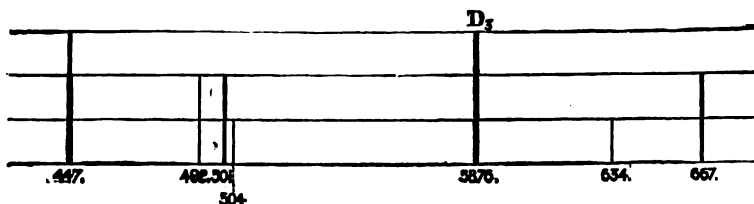


FIG. 2.
Diagram showing order in which lines appear in spectrum of vacuum tube when bröggerite is heated.

Working on these lines, the spectrum of the spark at atmospheric pressure, passing through the gas, or gases, distilled from bröggerite, has been studied with reference to the special lines C (hydrogen), D_3 , 667, and 447.

The first result is that all the lines do not vary equally, as they should do if we were dealing with a simple gas.

The second result is that at the lowest tension 667 is relatively more brilliant than the other lines; on increasing the tension, C and D_3 considerably increase their brilliancy, 667 relatively and absolutely becoming more feeble, while 447, seen easily as a narrow line at low tension, is almost broadened out into invisibility as the tension is increased in some of the tubes, or is greatly brightened as well as broadened in others (fig. 1).

The above observations were made with a battery of five Grove cells; the reduction of cells from 5 to 2 made no difference in the phenomena except in reducing their brilliancy.

Reasoning from the above observations, it seems evident that the effect of the higher tension is to break up a compound, or compounds, of which C, D_3 , and 447 represent constituent elements; while, at the same time, it would appear that 667 represents a line of some compound which is simultaneously dissociated.

glorious yellow effulgence of the capillary, while the current was passing, was a sight to see. But after this had gone on for some time, while the coincidence of the yellow line with D_3 of the chromosphere was being inquired into, the luminosity of the tube was considerably reduced, and the colours in the capillary and near the poles were changed. From the capillary there was but a feeble glimmer not of an orange tint, while the orange tint was now observed near the poles, the poles themselves being obscured by a coating on the glass of brilliant metallic lustre.

After attempting in vain for some time to determine the cause of the inversion of D_3 and 447 in various photographs I had obtained of the spectra of the products of distillation of many minerals, it struck me that these results might be associated with the phenomena exhibited by the tube, and that one explanation would be rendered more probable if it could be shown that the change in the illumination of the tube was due to the formation of platinum compounds, platinum poles being used. On May 21st I accordingly passed the current and heated one of the poles, rapidly changing its direction to assure the action of the negative pole, when the capillary shortly gave a very strong spectrum of hydrogen, both lines and structure. A gentle heat was continued for some time and apparently the pressure in the tube varied very con-

* A Paper read before the Royal Society.

siderably, for as it cooled the hydrogen disappeared and the D_2 line shone out with its pristine brilliancy. The experiment was repeated on May 24th and similar phenomena were observed.

ON THE OCCLUSION OF OXYGEN AND HYDROGEN BY PLATINUM BLACK.*

(PART I.)

By LUDWIG MOND, F.R.S., WILLIAM RAMSAY,
Ph.D., F.R.S., and JOHN SHIELDS, D.Sc., Ph.D.

THE authors describe some preliminary experiments on the occlusion of oxygen and hydrogen by platinum sponge and foil, which in general confirm the results obtained by Graham. At most only a few volumes of these gases are occluded by the more coherent forms of platinum.

After giving details of what they consider the best method of preparation of platinum black, they next describe some experiments which had for their object the determination of the total quantity of water retained by platinum black, dried at 100°C ., and the amount of water which can be removed from platinum black at various temperatures in vacuo. As the result of these experiments they find that platinum black dried at 100° retains in general 0.5 per cent. of water, and this can only be removed in vacuo at a temperature (about 400°) at which the black no longer exists as such, but is converted at least partially into sponge. At any given temperature the water retained by platinum black seems to be constant. The density of platinum black dried at 100°C . is 19.4, or allowing for the water retained by it at this temperature, 21.5.

The amount of oxygen given off by platinum black at various temperatures was determined. Altogether it contains about 100 volumes of oxygen; the oxygen begins to come off in quantity at about 300°C . in vacuo, and the bulk of it can be extracted at 400°C ., but a red heat is necessary for its complete removal. Small quantities of carbon dioxide were also extracted, chiefly between 100 — 200°C .

In determining the quantity of hydrogen occluded by platinum black the authors have carefully distinguished between the hydrogen which goes to form water with the oxygen always contained in platinum black, and that which is really absorbed by the platinum *per se*. Altogether about 310 volumes of hydrogen are absorbed per unit volume of platinum black, but of this 200 volumes are converted into water, or only 110 volumes are really occluded by the platinum. Part of it can be again removed at the ordinary temperature in vacuo; by far the larger portion can be extracted at about 250 — 300°C ., but a red heat is necessary for its complete removal. The amount of hydrogen absorbed by platinum is very largely influenced by slight traces of impurity, probably grease or other matter which forms a skin over the platinum.

Platinum black in vacuo absorbs a certain quantity of hydrogen. On increasing the pressure of the hydrogen up to about 200—300 m.m. a further quantity is absorbed, but after this pressure is almost without effect. By increasing the pressure from one atmosphere up to four and a half atmospheres, only one additional volume of hydrogen was absorbed. On placing platinum black charged with oxygen in an atmosphere of oxygen, and increasing the pressure to the same extent, eight and a half additional volumes were, however, absorbed.

Platinum black charged with hydrogen and placed in an atmosphere of hydrogen kept approximately at atmospheric pressure, and platinum black charged with oxygen and confined in an atmosphere of oxygen behave quite differently when heated. In the former case hydrogen is

immediately expelled on raising the temperature, whilst in the latter case oxygen is steadily absorbed until a temperature of about 360°C . (the temperature of maximum absorption) is reached, when, on further heating, oxygen begins to come off again.

Incidentally it was noticed that mercury begins to combine with oxygen at 237°C ., and that a mixture of platinum black and phosphorus pentoxide absorbs oxygen at a high temperature, probably with the formation of a phosphate or pyrophosphate.

In the discussion of the results special reference is made to the work of Berliner and Berthelot, and it is pointed out that there is not sufficient evidence for the existence of such chemical compounds as Pt_{30}H_2 and Pt_{30}H_4 . Moreover, the authors are of opinion that the heats of combination of hydrogen and platinum as determined by Berthelot and Favre are valueless, and that the heat which they measured is due, for the most part if not entirely, to the formation of water by the oxygen always contained in platinum black. It has yet to be proved that the absorption of hydrogen by pure platinum black is attended by the evolution of heat, and as regards the formation of supposed true chemical compounds, solid solutions, or alloys, the authors prefer to wait until sufficient data have been accumulated for an adequate inquiry before coming to any definite conclusion.

ON THE FORGING OF FLAT CRUCIBLE STEEL INGOTS FOR TOOL MANUFACTURE.

By SERGIUS KERN, M.E.

In the CHEMICAL NEWS (lxxi., p. 187) I gave a description of my system of casting crucible steel ingots. I may add that the forging of ingots is going well, and the loss through piping is remarkably small. Capt. Trouchanoff, manager of the forge of the New Admiralty, St. Petersburg, thus reports about my system:—

"In many cases, during the manufacture of various tools at works, having for such work crucible steel ingots, it is much preferable to use flat ingots, cast by Mr. Kern's system."

St. Petersburg, June 2, 1895.

NOTE ON "STANDARD" ACID SOLUTIONS.

By H. DROOP RICHMOND.

DR. PERMAN and MR. JOHN describe (CHEMICAL NEWS, lxxi., 296) a new method for standardising solutions. Seeing that it has been used for at least eight years, and has been exhaustively studied by Rimbach (*Ber.*, xxvi., 164), who even used the method of titration of borax with acid, methyl orange being employed as indicator, for the determination of the atomic weight of boron, it is not correct to call it a new method.

The process is certainly very convenient, and much more accurate than the results of Messrs. Perman and John would indicate—e.g., a difference between duplicates of 0.4 per cent is shown; certain precautions are, however, necessary, to which the authors have not drawn attention. From the very fact of the method being described as new, it is evidently not so well known as it should be, and consequently no excuse need be offered for describing the necessary precautions.

It does not do to trust to the borax having the composition $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. The water of crystallisation should be estimated at the time of weighing out the borax; half-an-hour's ignition in a muffle is usually necessary to drive off all the water.

Commercial methyl-orange sometimes contains an

* Abstract of a paper read before the Royal Society.

objectionable brown colouring-matter, which can, however, be removed by one or two crystallisations from alcohol.

The solution of the borax should not be too strong; about 20 c.c. of water for each 1 grm. is convenient. If too large a proportion of neutral salts be present, the delicacy of the end reaction is impaired; this is probably the reason for the difference of 0.4 per cent in Messrs. Perman and John's results.

An excellent method of preparing standard sulphuric acid is to weigh a quantity of acid of known density (best about 96 per cent H_2SO_4), and dilute to a definite volume. The excellent work of Pickering (*Journ. Chem. Soc.*, lvii., p. 64) has given us data for the calculation of the strength of sulphuric acid from the density with great exactitude.

It must be remembered that, whether the sulphuric acid is weighed, or titrated with borax, or estimated with barium chloride, that the strength of our acid is expressed in terms of the actual sulphuric acid present; when we come to use this acid in practice, employing, as is very frequently the case, phenolphthalein as indicator, we have not only the acidity of the sulphuric acid, but also that of the dissolved carbonic acid, entering into the reaction. We are usually very careful in keeping our alkali solutions free from carbonates (where they are of minor importance, as the alkali solution is always standardised against acid solution), while we utterly neglect all precautions for keeping our acid solutions free from carbonic acid.

The atomic weight of boron seems to be from the determinations of Ramsay and Aston, and Rimbach, who both used borax, 10.95, and, adopting this and the atomic weights given by Clarke for sodium, oxygen, hydrogen, and sulphur and chlorine, 1 grm. of anhydrous borax is equal to 0.48575 grm. sulphuric acid and 0.36115 grm. hydrochloric acid.

THE DETERMINATION OF WATER IN COMMERCIAL SAMPLES OF SULPHATE OF AMMONIA.

By JOHN HUGHES, F.I.C.

It is not generally usual to state the percentage of water present in commercial samples of sulphate of ammonia.

Occasionally chemists are asked to do so, also to state the amount of acidity, and in such cases the figures are given; but usually only the percentage of nitrogen equal to ammonia is reported.

The writer thinks that it would be desirable and useful that the percentage of water lost at 212°F ., and the acidity expressed as H_2SO_4 , should always accompany the figures for nitrogen and ammonia on the certificate.

Sulphate of ammonia, when ground up in a mortar, rapidly loses moisture in a hot dry atmosphere.

Consequently, in order to make a correct report on the percentage of nitrogen contained in the sulphate of ammonia in its natural state as received, it becomes necessary to make two water determinations. One in the sample as turned out in its rough damp state before grinding, and one in the finely ground portion prepared for the purposes of analysis; the analytical results being afterwards calculated into the natural state as received and reported accordingly.

The question of water really is a most important one, bearing in mind the commercial value of the material and the fact that every 1 per cent of water lost represents an increase of 0.25 per cent of ammonia.

It is true that the introduction of centrifugal machines has largely reduced the proportions of water and acidity in the sulphate of ammonia as sent out; but there is still sufficient difference between the dampness, respectively at the top and the bottom of the bags, to make the sampling a matter of great importance.

The following twelve samples, representing one delivery of yellow sulphate of ammonia, were furnished the writer by a large London manure firm, six bags being selected, and samples drawn respectively, from the top and bottom of each.

The proportions of water and acidity were then carefully determined as above suggested, a weak solution of litmus being employed as indicator in titration for acidity.

Top Samples.

	Water as received.	Water as analysed.	Water lost during preparation.	Free acid calculated as H_2SO_4 .
1	1.98	1.26	0.72	0.97
2	1.81	1.42	0.39	0.63
3	1.59	1.20	0.39	0.65
4	0.87	0.48	0.39	0.81
5	1.12	0.50	0.62	0.79
6	1.32	0.72	0.60	1.03
Average ..	1.45	0.93	0.52	0.81

Bottom Samples.

	Water as received.	Water as analysed.	Water lost during preparation.	Free acid calculated as H_2SO_4 .
1	2.62	1.64	0.98	1.24
2	2.65	1.94	0.71	0.81
3	2.53	1.76	0.77	0.80
4	3.14	2.12	1.02	1.22
5	1.97	1.24	0.73	0.71
6	2.39	1.84	0.55	1.07
Average ..	2.55	1.76	0.79	0.97

It will be noticed that the differences are considerable; the top samples being much drier than the bottom ones, in No. 4 the difference being as much as 2.27, representing 0.56 ammonia; and the water lost during preparation amounting in some cases to over 1 per cent, representing 0.25 ammonia.

Of course this loss during preparation will vary with the degree of grinding, the time exposed, and the temperature and humidity of the atmosphere.

The following figures in seven other samples, each representing a different delivery and analysed at a different time, will serve to indicate the variation that may be expected:—

Colour.	Water as received.	Water as analysed.	Water lost during preparation.	Free acid calculated as H_2SO_4 .
White	2.20	1.80	0.40	0.29
Yellow	1.94	1.50	0.44	0.31
Yellow	2.31	2.06	0.25	0.15
Grey	2.96	2.74	0.22	0.38
White	1.70	1.10	0.60	0.15
White	1.90	1.40	0.50	0.23
White	1.89	1.32	0.57	0.25
Average ..	2.13	1.70	0.42	0.25

The amount of acidity is of importance, because if not excessive, say not more than 0.5 per cent, the sulphate of ammonia can safely be shipped in double bags instead of in the more expensive casks which were formerly used.

If the certificate of the analyst contains information as to the percentage of water and acidity, in addition to the figures for nitrogen equal to ammonia, the identity of the sample with the bulk can be more readily established than when the figures for ammonia only are stated.

In a paper published in the *CHEMICAL NEWS* (lxii., p. 325) the writer drew attention to the importance of stating the percentage of water when reporting on the quality of wool waste, and pointed out that the omission to do so, and to state the percentage of nitrogen for the sample as received, had no doubt caused the serious differences between analysts, which up to that date was of frequent occurrence, but which since then have disappeared.

He trusts that this communication may be received by analysts in a similar favourable manner.

79, Mark Lane, London, E.C.,
June 20, 1895.

ON THE NATURE AND COMPOSITION OF THE COMMERCIAL RUSSIAN KEROSENE.

By J. ALFRED WANKLYN and W. J. COOPER.

IN December, 1893, and in January, 1894, in the *Philosophical Magazine* and in the *CHEMICAL NEWS*, the announcement was made that, by most persistent and methodical fractionation, a homologous series of hydrocarbons had been separated into its terms, and that its terms differed from one another, not by the common increment 14, but by the common increment 7. In following papers we have disclosed that the hydrocarbons in question are the hydrocarbons existing in mixture in the commercial Russian kerosene, and have published further details.

On the present occasion we publish a tabular *resumé* of the work. The hydrocarbons of this series we have named keroses, and in the table the Roman numeral expresses the number of atoms of carbon (the atomic weight of carbon being 6) in the molecule of the kerosene.

We have obtained an acetic compound of almost every individual kerosene, one molecule of kerosene being united with one little molecule of acetic acid. The preparation of such compounds was described in the *CHEMICAL NEWS* of May 24 (vol. lxxii., p. 250).

	V. D.	Sp. gr.		Boils at 15°5 C.	Boils at °C.	Percentage of Hydrocarbon in Acetic K.	
		Theory.	Found.			Theory.	Found.
Ay	xiii.	3'144	3'192	0'7350			
As	xiv.	3'386	3'43	0'7460	85	62'04	62'33
Aa	xv.	3'63	3'69	0'7510	96'5	63'63	62'75
Ab	xvi.	3'87	3'91	0'7576	106	65'12	64'48
B	xvii.	4'11	4'08	0'7606	116'5	66'48	65'9°
Bb	xviii.	4'35	4'36	0'7711	127	67'74	67'84
Bc	xix.	4'59	4'59	0'7768	138	68'91	69'06
C	xx.	4'84	4'84	0'7843	148	70'00	69'70
D	xxi.	5'08	5'02	0'7975	158	71'01	70'94
Dd	xxii.	5'32	5'20	0'8057	168	71'96	72'00*
De	xxiii.	5'56	5'51	0'8090	176	72'87	72'99
E	xxiv.	5'80	5'77	0'8185	186	73'68	74'01
F	xxv.	6'04	6'08	0'8240	197	74'47	74'64
Ff	xxvi.	6'28		0'8255	205	75'21	75'28
G	xxvii.	6'52	6'53	0'8270	214	75'90	77'02
Gg	xxviii.	6'77	6'82	0'8287	222	76'56	77'31
H	xxix.			0'8338	230	77'18	77'53
Hh	xxx.			0'8392	237	77'77	77'53
I	xxxi.			0'8430	246	78'34	78'34°
K	xxxii.			0'8470	253	78'87	79'43
L	xxxiii.			0'8520	260	79'38	79'95
M	xxxiv.			0'8560	267	79'87	79'83
N	xxxv.			0'8590	274	80'33	80'63°
O	xxxvi.			0'8603	280	80'77	80'55

* Mean.

Z residue, dark coloured liquid, sp. gr. 0'880, amounting to about 13 per cent of the total kerosene.

The circumstance that the specific gravity of the liquid kerosene always rises as the molecule increases in weight will be noted. This rise is small, but invariable, and affords an argument in favour of there being substantially only one hydrocarbon series present in the Russian kerosene of commerce. Apparently, however, the rise (though it always occurs) is not always equal in extent.

The boiling-points of the keroses must be looked upon as to some extent provisional. We are in possession of the liquids and have not used them up in making the acetic compounds, and we purpose to re-determine the boiling-points.

A REFORM IN CHEMICAL, PHYSICAL, AND TECHNICAL CALCULATIONS.

By C. J. HANSSEN, C.E.

(Continued from p. 309).

The Dynamic Equivalent of Heat.

If 1 cbm. hydrogen of atmospheric pressure and 273° N. absolute temperature is heated to 546° N. absolute (273° increase of temperature), it expands to 2 cbm. of 1 atmosphere pressure; it would, enclosed in a cylinder with movable piston of 1 sq. m. area, by expanding, move the piston 1 m. against the pressure of the atmosphere; and, consequently, as atmospheric pressure upon 1 sq. m. is = 10330'442 kg., perform 10330'442 m.kgr. of work.

To heat 1 cbm. of hydrogen 273° N., is required—

At constant pressure 273° × 17/56 cal.
At constant volume 273° × 12/56 "

The difference 273° × 5/56 cal. = 1365/56 = 24½ calor. = 24'375 cal. has performed 10330'442 m.kgrs. of work; consequently,—

$$1 \text{ cal.} = \frac{10330'442}{24'375} = 423'813 \text{ m.kgrs.}$$

Exactly the same result do we get by calculating with oxygen, nitrogen, or other simple gases, and likewise with CO and with air; but, by making the calculation with a compound gas which, in combining, has contracted its volume, the result is *apparently* different.

For carbon dioxide (of which 1 cbm. contains 1½ cbm. of simple gases, are required—

At constant pressure 273° × 51/112 cal.
At constant volume 273° × 36/112 "

The difference 273° × 15/112 cal. = 4095/112 = 36½ calor., moves the piston 1 m., and performs 10330'442 m.kgrs. of work. This compound gas has consequently absorbed exactly 1½ times as much heat as the simple gas, to perform the same amount of work, but in this case, ½ of the 36½ cal. = 18½ cal., is absorbed to counteract the chemical affinity which contracted 1 cbm. O and ½ cbm. C into 1 cbm. CO₂, and the remaining ½ × 36½ = 24½ calor. perform the same amount of dynamic work as in the first case. The same calculation made with many other gases, gives, with absolute accuracy, the same result: 1 calor. = 423'813 m.kgrs.

Water evaporates in vacuum at 219½° N. absolute (−53½° N.), because, by very careful investigation of Regnault's experiments on evaporation of water, the author finds that in all cases, from the highest to the lowest temperature,—

$$\frac{W \times T}{P} = 219\frac{1}{2}$$

Here T denotes the absolute temperature of the steam (°N.), W the weight of the steam (kgr. per cbm.), and P the absolute pressure of steam in atmospheres; and for all weights, pressures, and temperatures of steam ascertained by those experiments, the coefficient—

$$219'375 = 219\frac{1}{2} = \frac{1755}{8}$$

is the result. For every known pressure and weight of steam we consequently find the corresponding absolute temperature, T, by the equation—

$$T = \frac{1755 P}{8 W} = \text{° N. absolute.}$$

Aëiform substances increase in weight in *inverse* proportion to their absolute temperature; consequently, vapour of water (steam) of 1 atmosphere and 273° N. absolute, of which 1 cbm. weighs 45/56 kg., would weigh 56/56 kg. (= 1 kg.) if cooled, as proportion—

$$56 : 45 = 273^\circ \text{ absolute} : 219\frac{1}{2}^\circ \text{ N. absolute.}$$

If at $219\frac{1}{2}^{\circ}$ N. absolute 1 cbm. steam of 1 atmosphere weighs 1 kg., then 1 cbm. of 0.00000001 atmosphere must weigh 0.00000001 kg. If we insert these values for P and W in the equation, we find the temperature—

$$T = \frac{1755 \times 0.00000001 \text{ atm.}}{8 \times 0.00000001 \text{ kg.}} = 219\frac{1}{2}^{\circ} \text{ N. abs.} = -53\frac{1}{2}^{\circ} \text{ N.}$$

where water will commence to evaporate in absolute vacuum. By increasing the temperature, the pressure of steam increases in the following ratio:—

Atmospheres.	Absolute. °N.	°N.
0.00000001	219 $\frac{1}{2}$	= -53 $\frac{1}{2}$
0.0000001	220 $\frac{1}{2}$	= -52 $\frac{1}{2}$
0.000001	220 $\frac{1}{2}$ + ($\frac{1}{2}$ × 1.50) = 225 $\frac{1}{2}$	= -47 $\frac{1}{2}$
0.00001	225 $\frac{1}{2}$ + ($\frac{1}{2}$ × 1.51) = 232 $\frac{1}{2}$	= -40 $\frac{1}{2}$
0.0001	232 $\frac{1}{2}$ + ($\frac{1}{2}$ × 1.54) = 243	= -30
0.001	243 + ($\frac{1}{2}$ × 1.54) = 259	= -14
0.01	259 + ($\frac{1}{2}$ × 1.54) = 283	= +10
0.1	283 + ($\frac{1}{2}$ × 1.54) = 319	= +46
1.0	319 + ($\frac{1}{2}$ × 1.54) = 373	= +100
10.0	373 + ($\frac{1}{2}$ × 1.54) = 454	= +181
100.0	454 + ($\frac{1}{2}$ × 1.54) = 575 $\frac{1}{2}$	= +302 $\frac{1}{2}$

By calculating the temperatures due to 83 intermediate pressures, and of these construct a diagram, the author obtained a curve, which agrees well with Regnault's experiments; in fact, so well that the small deviations must be caused by experimental errors.

The specific heat of liquid water, as usually taken, = 1; the specific heat of ice (which is condensed H₂O at constant volume), of vaporised water (steam), and of H₂O gas is = 0.4. Melting 1 mgr. of ice absorbs 79 $\frac{1}{2}$ calors, which become latent. Evaporating 1 mgr. of liquid water absorbs 8 × 79 $\frac{1}{2}$ = 634 calors., which become latent, minus 0.1 cal. per °N. absolute temperature of the steam generated.

Heat required to Melt Ice, Vaporise and Decompose Water.

1 mgr. solid H₂O (ice) at absolute zero of temperature (0° abs.) contains no heat;—

Heated to 273° abs. (+0° N.) it contains 273 × 0.4 cal.	= 109.20 calors.
Latent heat of liquefaction of ice	= 79.25 "

Total heat in 1 mgr. liquid water of 273° N. abs. (0° N.) = 188.45 "

Latent heat of evaporation per 1 mgr. liquid water of 273° N. absolute converted into vapour of 273° N. abs., 634 cal. - (273° × 0.1 cal.) = 606.70 "

Total heat in 1 mgr. steam of 273° N. absolute (0° N.) = 795.15 "

Heat required to evaporate 1 mgr. liquid water of 273° N. absolute (0° N.) into steam of atmospheric pressure and 373° N. absolute (100° N.)—

Latent heat of evaporation, 634 cal. - (373° × 0.1 cal.)	= 596.70 calors.
1 mgr. steam heated 100° N. and 0.4 cal.	= 40.00 "

To convert 1 mgr. water of 0° N. into steam of 100° N. requires 636.70 "

To evaporate 1 mgr. water of 273° N. absolute into steam of 10 atmospheres pressure and 454° N. absolute (181° N.), is required:—

Latent heat of evaporation 634 cal. - 454° × 0.1 cal.)	= 588.60 calors.
1 mgr. steam heated 181° N. and 0.4 cal.	= 72.40 "

To convert 1 mgr. of water of 273° N. absolute (0° N.) into steam of 181° N. requires 661.00 "

These examples, which also hold good for lower and higher pressures, show that although $\frac{1}{2}$ = 0.4 calors. are required to raise the temperature of 1 mgr. saturated steam 1° N., only 0.3 calors. are to be supplied from outer sources of heat, while 0.1 calors., taken from the 634 calors. latent heat of evaporation, is converted into sensible heat or temperature.

These 0.3 calors. are, in the process of evaporation, applied thus:—

$\frac{1}{2}$ = 10/90 calors. per 1° N. is used to overcome atmospheric resistance.

$\frac{1}{3}$ = 5/90 calors. is used to overcome chemical affinity of H and O.

$\frac{1}{6}$ = 12/90 calors. is used to overcome physical cohesion of atoms.

27/90 calors. = 0.3 calors. per 1° N. to be supplied from outer sources of heat.

The 79 $\frac{1}{2}$ calors. + 634 calors. = 713.25 calors. latent melting and evaporating heat required to evaporate 1 mgr. ice 0° N. abs., decrease 0.3 calors. for every 1° N. temperature above absolute zero; consequently, the absolute temperature, where water is converted into permanent H₂O gas, is found by proportion:—

$$0.3 \text{ cal. : } 713 : 25 \text{ cal.} = 1^{\circ} \text{ N. : } 2377.5^{\circ} \text{ N. absol.}$$

Heating 1 mgr. H₂O at constant pressure 1° N. requires $\frac{1}{2}$ calors.; consequently, raising the temperature from 0° absolute to 2377.5° N. absolute requires—

$$2377.5^{\circ} \text{ N.} \times \frac{1}{2} \text{ cal.} = 1347\frac{1}{2} \text{ calors.,}$$

which is equal to—

$$(1+8+8) \times 79\frac{1}{2} \text{ cal.} = 17 \times 79\frac{1}{2} \text{ cal.} = 1347\frac{1}{2} \text{ calors.}$$

Water Decomposed into Simple Hydrogen and Oxygen Gas.

If we heat 1 mgr. of solid water (ice), of 0° N. absolute, to 14 × 2377 $\frac{1}{2}$ ° N. absolute = 3566 $\frac{1}{2}$ ° N. absolute, we have brought it to the temperature where the molecules of H₂O decompose into simple H and O gas. To heat 1 mgr. of solid water of 0° N. absolute to this temperature are required—

$$3566\frac{1}{2}^{\circ} \text{ N.} \times \frac{1}{2} \text{ cal.} = 2020\frac{1}{2} \text{ calors.}$$

But in order actually to split the H₂O molecules into simple hydrogen and oxygen gas of 3566 $\frac{1}{2}$ ° N. absolute temperature, are required per 1 mgr.:—

$$2 \times 2020\frac{1}{2} \text{ calors.} = 4041\frac{1}{2} \text{ calors.,}$$

which is equal to—

$$3 \times (1+8+8) \times 79\frac{1}{2} \text{ cal.} = 3 \times 17 \times 79\frac{1}{2} = 51 \times 79\frac{1}{2} = 4041\frac{1}{2} \text{ calors.}$$

By this operation, the 1 mgr. of ice of 0° N. absolute is dissolved into $\frac{1}{2}$ mgr. of hydrogen and $\frac{1}{2}$ mgr. of oxygen, which, at that temperature (3566 $\frac{1}{2}$ ° N. absolute), are = 634/39 cbm. hydrogen and 317/39 cbm. oxygen = total 951/39 cbm. = 24 $\frac{1}{3}$ cbm. of simple gases of 3566 $\frac{1}{2}$ ° N. absolute and atmospheric pressure.

As dissolving 1 mgr. of ice of 0° N. absolute temperature into its components requires 4041 $\frac{1}{2}$ calors., it follows that the combustion of $\frac{1}{2}$ mgr. hydrogen with $\frac{1}{2}$ mgr. oxygen (which form 1 mgr. of water), must likewise develop 4041 $\frac{1}{2}$ calors.; and, consequently, the combustion of 1 mgr. of H with 8 mgrs. of O, forming 9 mgrs. of water, will produce:—

9 mgrs. × 4041 $\frac{1}{2}$ calors. absolute = 36375.75 calors. total heat 9 mgrs. of water of 273° N. abs.

$$\text{contain } 9 \times 188.45 \text{ cal.} = 1696.05 "$$

Consequently—

1 mgr. hydrogen burnt with oxygen produces 34679.70 "

if the initial temperature of the gases has been 273° N. absolute, and the products of combustion are cooled down to that temperature; and the temperature of combustion of H with O is 3566 $\frac{1}{2}$ ° N. absolute, and 3566 $\frac{1}{2}$ ° - 273° = +3293 $\frac{1}{2}$ ° N.

Pressure exerted by Freezing Water.—This pressure the author finds to be = 1904 atmospheres.

Water hermetically enclosed in a strong vessel remains liquid at -24° C. (249° C. absolute), as proved by M. Bousingault's experiment; and probably it remains liquid at all lower temperatures down to 2198° N. absolute if expansion is absolutely prevented.

(To be continued.)

3, Valdemaragade, Copenhagen, V.
May 6, 1895.

SPECTROSCOPIC STUDY OF THE CARBONS OF THE ELECTRIC FURNACE.

By M. DESLANDRES.

H. MOISSAN has recently announced (*Comptes Rendus*, cxix., p. 1245) that the carbons of the arc in his electric furnace are purified by the passage of currents of great intensity, and are thus freed from the foreign matters which they always contain in notable proportion.

We know that it is very difficult to purify charcoal by chemical means. This property of the electric furnace is therefore important, and in particular it interests spectroscopists who in their researches of qualitative analysis often employ electrodes of carbon as pure as possible. I have thus been led to a special study of the carbons of the electric furnace, to ascertain on the one hand their value in analysis, and on the other to determine the complete spectrum of pure carbon.

Moissan having placed at my disposal two carbon poles, a positive and a negative (length of 0.20 metre and thickness of 0.05 metre), which had served in his experiments, I took from each pole small portions of charcoal at variable distances from the arc (0.15 , 0.10 , 0.05 , and 0.01). Now the specimens the most remote from the arc still showed the rays of the ordinary impurities of charcoal, i.e., the alkaline and earthy-alkaline metals, with copper, iron, and silicon; but on approaching the arc, the rays of the impurities gradually diminished and finally disappeared, excepting only the rays of calcium, which, although much reduced, are still visible; this fact being due to the proximity of the sides of the furnace consisting of lime. These sides are themselves volatilised by very intense currents.

This purification of carbon seems to depend on a purely physical cause; the foreign matters, much more volatile than the carbon, are thrown off in the state of vapour. In fact, the purest parts of the two poles are the caps ("mushrooms," as the author calls them), which are termed at the negative pole of transportation from the positive pole to the opposite pole. With one of the caps the following spectrum of carbon has been obtained, containing fewer rays than the similar spectrum published by Liveing and Dewar, Hartley and Adeney, Eder and Valenta:—

Intensities.	Wave-lengths.
8	426.70
5	392.17
4	391.97
2	316.83
1	316.57
2	299.34
1	296.77
8	283.75
8	283.69
4	274.75
3	264.12
8	251.19
8	250.79
10	247.88
8	229.70

—*Comptes Rendus*.

RELATION BETWEEN VALENCE AND ATOMIC VOLUME.

By HOLLAND CROMPTON.

In these (*Berichte*, xxvii., p. 2178 — compare also *Zeit. f. Anorg. Chemie*, viii., p. 127) J. Traube shows the existence of a relation between valence and atomic volume, and that the "change of valence of an elementary atom is mostly attended with a change of the atomic volume," the atomic volume here in question being the atomic solution volume.

In a memoir which I have recently submitted to the Chemical Society of London, I showed that there exists an intimate relation between the molecular (or atomic) latent heat of fusion, ρ , and the valences of the atoms present in the molecule, so that it is possible, by means of certain simple rules laid down in the memoir, to deduce from the valences a number ΣV , such that $\rho T_0 = C \Sigma V$, where T_0 signifies the melting-point in absolute degrees of temperature, and C is a constant which has the same value for all substances. The connection of the latent heat of fusion with the valence leads to the following confirmation of Traube's results:—

In the year 1870 Goldberg (*Compt. Rend.*, lxx., p. 1349) established the following relation between the vapour-pressure p' of a solution of the melting-point T in absolute temperature, and the vapour-pressure p of the solvent of the melting-point T_0 :

$$\ln \frac{p}{p'} = \frac{R}{T_0} \frac{T_0 - T}{T}$$

where R is the constant of the Boyle-Gay Lussac equation. It may now be shown, thermo-dynamically (Nernst, "Theoret. Chemie," p. 125), that if P is the osmotic pressure of a solution in which a change of volume $d\upsilon$ is effected by the removal of dx grms. of the solvent, the equation holds good:—

$$P = \frac{dx}{d\upsilon} RT \ln \frac{p}{p'}$$

If this formula is combined with that of Goldberg, we have—

$$\frac{P}{T_0 - T} \frac{d\upsilon}{dx} = \frac{p}{T_0} = C \Sigma V.$$

Here $d\upsilon/dx$ is the volume occupied by 1 mol. of the solvent in the given solution; therefore the molecular volume of the solvent, or that part of the solution which separates out at the point of fusion, is the dissolved salt in solutions near on saturation for which Traube's relation is applicable. Consequently the molecular volume of a salt is a function of the valences of the atoms forming the molecule.—*Berichte*, xxviii., No. 2, p. 148.

EXAMINATION OF BLOOD-PIGMENT AS TO ITS POWER OF ABSORBING THE VIOLET AND ULTRA-VIOLET RAYS.*

By H. GRAEBE.

As the source of light, the author used in part sunlight and in part the light of the electrical spark, the spectrum of which extends to six or seven times the length of the visible spectrum beyond H. The induction current of a Ruhmkorff apparatus was excited by four Bunsen elements, and served to charge a battery of nine Leyden jars. In most of the investigations an iron and a copper pole were used. The division of the spectrum thus obtained was effected by comparison with the photograph of the spectrum of a spark obtained under exactly the same

* An Inaugural Dissertation at Dorpat, 1892.

conditions, and which had passed between the poles of an alloy of lead, tin, and cadmium; the wave-lengths of the lines of the latter spectrum were obtained from a paper of Hartley's (*Phil. Trans.*, 1885). As the achromatic collimator lens generally employed for photographs extending beyond H (consisting of a plano-convex lens of calcareous spar and a bi-convex quartz lens) was not at hand, the author used a chromatic quartz lens, which certainly showed only one part of the spectrum distinctly, whilst the other parts could be successively adjusted sharply by a corresponding rotatory movement of the quartz prism. The displaceable slit of the spectroscopic constructed by the author was placed, accurately centred, at double the focal distance of the lens. Immediately behind the lens was the prism, so adjusted on a movable axle that its requisite rotation could be regulated by means of a scale and index. As troughs there were used vessels of rock crystal, with plane parallel sides.

For the proofs there were used the Lumière's ordinary silver-bromide plates. The time of exposure varied according to the state of the sunlight, from 30 to 120 seconds, and for the light of the spark between 200 and 100 electric discharges. The proofs were developed with iron oxalate, and fixed with a 15 per cent solution of hyposulphite.

Soret (*Comptes Rendus*, xcvi., 1269) had observed the absorption of blood in the violet, and mentions also two absorption bands, "one of which, at Cd_{12} , is probably due to hæmoglobine, whilst the other, at Cd_{17} , is evidently produced by the serum." D'Arsonval has also recognised the absorption band of oxyhæmoglobine in the violet. The author, whilst making use of these former researches, has studied, by the aid of photographs, the absorptions of oxyhæmoglobine, hæmoglobine, methæmoglobine, cyanmethæmoglobine, sulphomethæmoglobine, carbonic oxide hæmoglobine, hæmatine, hæmochromogen, and hæmine, in the violet and ultra-violet. He observed the following absorptions:—

a. *Oxyhæmoglobine*.—A defibrinated solution of blood (20 per cent in a stratum of 1 m.m. in depth) absorbed the rays of the wave-lengths λ 465 to λ 358; a solution of 10 per cent absorbed from λ 450 to λ 381. If blood was diluted to 5 per cent the band extended from λ 440 to λ 396. A 1 per cent solution of blood showed in the yellow and the green merely a faint darkening, whilst there appeared a distinct band between λ 427 and λ 405. On further dilution the breadth of the absorption band decreases little; it declines in intensity, and entirely disappears at a dilution of 1 : 600.

b. *Hæmoglobine*.—For reducing oxyhæmoglobine there was used ammonium sulphide, or a solution of 1 part ferrous sulphate and 1 part tartaric acid in 10 parts of water, to which, shortly before use, 6 parts of "official liquid ammonia" are added. (Why does not the author express the strength of his ammonia in some standard universally understood?) Both reduction liquids must be as nearly colourless as possible before use, as they will otherwise darken the violet. A solution of hæmoglobine diluted to 10 per cent is impervious to the rays from λ 450 to λ 398, and one at 5 per cent from λ 447 to λ 408. The absorption in the violet here undergoes, in comparison with oxyhæmoglobine, a displacement towards the less refrangible part of the spectrum. The middle of the absorption band coincides with Fraunhofer's G line, and with a 1 per cent solution the absorption band—sharply defined on both sides—is visible in the violet between λ 437 and λ 417. Hæmoglobine has therefore, in the visible part of the spectrum, not one absorption band, but two bands. In the ultra-violet hæmoglobine is distinguished from oxyhæmoglobine merely by a stronger darkening of the most refrangible rays. A 6 per cent solution is transmissive to about λ 240.

c. *Methæmoglobine* was generally obtained by adding potassium ferricyanide to a solution of blood. The 10 per cent solution, in which the four absorption bands may still be distinctly recognised in the visible spectrum, ab-

sorbs in the violet from λ 440 to λ 358. The band seems washed out towards the ultra-violet on diluting the solution. If mixed with equal parts of distilled water, this solution absorbs from λ 430 to λ 382; if diluted to 1 per cent it allows all the light to pass through without hindrance as far as the violet rays from λ 420 to λ 400. In the ultra-violet, except a darkening of the most refrangible rays, there occurs no independent absorption.

By the addition of a small quantity of ammonia or potassium hydroxide the above-described image characteristic for methæmoglobine (in the so-called acid solution) disappears, and there appears a spectrum similar to that of oxyhæmoglobine, though the first absorption band is split into two.

Besides the two or three bands the author observed, on sufficient concentration, also an absorption band in the green between λ 555 and λ 525, which he has not found already described. The band in the violet in a 10 per cent solution extends beyond H to λ 375, and the side situate towards the red extends to λ 445. If the solution is diluted to 5 per cent only traces of absorption are to be found in the yellow and the green, whilst the space between the Fraunhofer lines G and H is darkened. In a 1 per cent solution the band recedes on one side to λ 415 and on the other to λ 405. In the invisible spectrum the only difference between methæmoglobine in an acid solution and in an alkaline solution is that by the latter the extreme ultra-violet is more strongly darkened.

d. *Cyanmethæmoglobine*, readily obtained by the addition of hydrocyanic acid to solutions of methæmoglobine, behaves like hæmoglobine; but in a 1 per cent solution, in a stratum of 1 m.m. in depth, absorbs the light rays from λ 580 to λ 523. The darkening of the violet extends beyond H, gradually fading from λ 450 to λ 381. On the addition of hydrocyanic acid the methæmoglobine band in the violet is therefore displaced towards the red. This phenomenon is observed more distinctly in a 1 per cent solution where the chief absorption is situate between λ 430 and λ 410. The photographic image of the ultra-violet shows that the most refrangible rays are absorbed by cyanmethæmoglobine, which increases with the increasing concentration of the solution.

e. *Sulphomethæmoglobine*, obtained by the action of hydrogen sulphide upon oxyhæmoglobine or hæmoglobine, besides the absorption band in the red, displays a band in the violet, and a darkening in the ultra-violet similar to that of methæmoglobine. A 10 per cent solution absorbs from λ 452 to λ 400; in a 5 per cent solution the limits of the band are seen at λ 440 and λ 408. A 1 per cent solution of blood treated with hydrogen sulphide absorbs from λ 427 to λ 415.

f. *Carbon monoxide hæmoglobine* likewise displays an absorption in the violet, even at so great a dilution that the bands in the yellow and the green are no longer visible. A 10 per cent solution of carbon monoxide blood shows on the photographic plate an absorption from λ 440 to λ 388. A 5 per cent solution absorbs from λ 430 to λ 407. If the solution contains 1 per cent of carbon monoxide blood the two characteristic bands in the yellow-green disappear, but the band in the violet is seen between λ 425 and λ 411.

g. *Hæmatine* was obtained by boiling an ammoniacal solution of blood, or one mixed with acetic acid. The absorptive power of acid hæmatine is exceedingly feeble for the violet rays on this side of H. Beyond H, both when the sun or the electric spark is used as a source of light, a very slight darkening, beginning at H and extending to about Cd_{12} .

The alkaline solution of hæmatine, even if much diluted, shows a band, certainly much washed out; its limits for a 10 per cent solution may be fixed between λ 432 and λ 348; a 5 per cent solution displays merely a darkening of the rays between λ 425 and λ 358. Besides an absorption of the extreme ultra-violet rays, there occurs in both cases a faint darkening at Cd_{12} and Cd_{17} .

h. *Hæmochromogen* is formed on treating solutions o

hæmatine with alkaline reductive agents. In the forensic demonstration of blood this substance plays a great part, on account of its uncommonly visible absorption bands; since solutions of blood-spots many years old, whose hæmatine bands would be visible only in the red, and visible only in very concentrated solutions if converted into hæmochromogen, show distinct absorptions in the green even when strongly diluted. Hæmochromogen is the more sharply characterised by its absorption band in the violet, which becomes visible on great dilution, and is therefore still more valuable for a judicial investigation. A solution at 1 per cent which transmits yellow and green light without hindrance, and consequently does not allow the recognition of the well-known absorption spectrum, still absorbs strongly the rays from λ 430 to λ 478. A 1 per cent solution causes the disappearance of the rays between G and H in the spectrum; a 10 per cent solution absorbs the rays from λ 443 to λ 400.

The most refrangible ultra-violet rays are strongly absorbed by hæmochromogen; a 4 per cent solution is impervious to rays more refrangible than Cd γ .

i. *Hæmin*, or hæmatine hydrochlorate, dissolved in methyl alcohol, shows in the violet an absorption band, the middle of which coincides with H. The hæmin solution is perfectly transmissive for ultra-violet light.

According to all the above the absorption band of the blood-pigment, as well as of its derivatives, is more permanent than the already more generally known and repeatedly described absorption bands in the visible part of the spectrum.

Hence it appears the more important that in hæmoglobine, carbon-monoxide hæmoglobine, and hæmochromogen, the absorption band in the violet enters into the visible part of the spectrum, and can be observed by the employment of diffused sunlight as a band defined on both sides. According to the observations of d'Arsonval the violet of the spectrum can be strongly extended towards the ultra-violet if the sun's direct rays or the light of an arc, concentrated by a lens of 10 c.m. in diameter with a very short focus, are allowed to fall into the slit of a spectroscopic, and the dazzling rays from red to blue are eliminated by means of a disc of deep blue glass. In this manner of observation prisms and lenses of glass may be used, which is of the greatest importance for practical detection.

In connection with this subject I may mention two remarks of A. Wetzel (*Chemiker Zeit.*, xiv., Rep. 87) on the recognition of blood containing carbon monoxide. He shakes gently 10 c.c. of the substance in question with 15 c.c. of a 20 per cent solution of potassium ferrocyanide and 2 c.c. of acetic acid of medium strength (1 vol. glacial acid and 2 vols. water), whereon the blood coagulates to a mass which gradually solidifies. Normal blood yields a black-brown clot, blood containing carbon monoxide a light red. Or we dilute 1 part blood with 4 parts water, add thrice the volume of solution of tannin, and shake round. The difference of colour between normal blood and that containing carbon monoxide increases on standing. After twenty-four hours the normal blood is grey, and that containing carbon monoxide crimson red. The difference is still to be distinguished after ten months. —*Zeitschrift für Anal. Chem.*, xxxiii., p. 771.

CORRESPONDENCE.

USE OF MINERAL OIL FOR EXCLUDING AIR IN PAVY TITRATIONS.

To the Editor of the Chemical News.

SIR,—I have delayed replying to Professor Brauner's letter published in the *CHEMICAL NEWS* (vol. lxxi., p. 292) until I had ascertained whether there was any foundation for his suggestion that one of the secretaries of the Che-

anical Society, "who alone are responsible for the abstracts in the *Proceedings*," had taken the astounding course of substituting the name "Allen" for that of "Soxhlet" in the abstract in question.

I am now in a position to inform your readers, upon official authority, that the Secretaries of the Chemical Society are not responsible for the above change of name, alleged by Professor Brauner to have been made.

Professor Brauner says that "instead of charging him with dishonest action, I should have sent him a copy of my paper, and given him private information." Unfortunately, at the time when the abstract appeared I was not aware of the existence of Professor Brauner, whom I know simply as the reader of certain papers before the Chemical Society on March 21st. I did all I could to communicate with Professor Brauner. I wrote to the Secretaries of the Chemical Society, informing them that the device had been previously described by me in three different journals, and I added: "The prior publication of the suggestion has evidently been overlooked by Professor Brauner, to whom I shall be obliged if you will forward this letter or communicate its substance." I am informed by the Secretaries that this request was promptly complied with, and have learned later that their letter did not receive any acknowledgment from Professor Brauner, who now states that he did not receive it.

As to the value of the use of mineral oil to exclude air in performing Pavy titrations, it is curious that the device is the only point in the paper communicated by Professor Brauner which the Secretaries of the Chemical Society appear to have considered worth including in the abstract which they prepared.—I am, &c.,

ALFRED H. ALLEN.

Sheffield, July 1, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxx., No. 24, June 17, 1895.

Professor Newcomb was elected as a Foreign Associate of the Academy, *vice* the late Prof. von Helmholtz. Herr Bachlund was elected a correspondent of the Section of Astronomy, *vice* the late R. Wolff; and Dr. Kowalewski correspondent of the Section of Anatomy and Zoology, *vice* the late M. Cotteau.

Law of Absorption of the Bands of the Spectrum of Oxygen.—J. Jansen.—The law is that the absorbent power of oxygen gas, relatively to these bands, is proportional to the thickness of the gaseous mass multiplied by the square of its density.

Combination of Free Nitrogen with the Elements of Carbon Disulphide.—M. Berthelot.—The author, whilst pursuing his researches on argon, has recognised the direct combination of free nitrogen with the elements of carbon disulphide. This combination takes place by the influence of electricity employed in the form of sparks or of the effluve. When operating on 15 c.c. of nitrogen at normal pressure, the volume having been increased to 25 c.c. by the addition of a small quantity of liquid carbon disulphide, carbon and sulphur are precipitated mixed with condensed carbon subsulphides; at the same time, nitrogen is fixed on the products.

New Combination of Argon: Synthesis and Analysis.—M. Berthelot.—(See p. 1).

Preparation and Properties of Pure Melted Molybdenum.—Henri Moissan.—(See p. 2).

Action of Phenyl Isocyanate upon the Campholic, Carboxyl-campholic, and Phthalic Acids.—A. Haller.

—The compounds obtained are the hydroxycampho-carbonic, iso-, and tere-phthalic acids.

Discovery of a Third Permanent Radiation of the Solar Atmosphere in the Gas of Clèveite.—H. Deslandres.—The permanent radiation of the solar atmosphere, λ 706.55, is emitted by the gas of clèveite, and it even seems to announce a new element common to the solar and terrestrial atmospheres. There is now only a single permanent radiation of the solar atmosphere which has not been recognised on the earth; that is the green ray λ 531.16, called the ray of the corona. It is distinguished as being peculiar to the most elevated regions of the atmosphere, which allows us to suppose that it belongs to a gas lighter than hydrogen.

Molecular Transformations of Chromic Hydrate.—A. Recoura.—The author has previously shown (*Ann. de Chim. et de Physique*, Series 7, vol. iv.) the existence of two varieties of chromium hydroxide, differing from each other by their capacity of saturation for acids. 1. The normal hydroxide is the precipitate produced by alkalis in the solution of a normal salt of chromium. It can fix 6 mols. of hydrochloric acid, evolving 41.4 cal. = 6×6.9 , and re-generating normal chromium chloride. The chromium hydroxide of the green solution is formed by decomposing by an alkali a solution of a salt of chromium previously rendered green by ebullition. It fixes only 4 mols. of hydrochloric acid. Chromium hydroxide, a hexatomic base, is transformed into a monatomic base, like the alkaline bases, after remaining for three hours in soda. If left for a longer time, it becomes a mixture of monatomic hydrate and of a hydrate of no atomicity.

Certain Basic Haloid Compounds of the Alkaline-Earthy Metals.—M. Tassilly.—The author has prepared and examined the strontium oxybromide and oxyiodide, and the corresponding barium salts.

Action of Heat upon the Double Alkaline Nitriles of the Metals of the Platinum Group: Compounds of Iridium.—A. Joly and E. Leidy.—The study of the double nitriles of iridium and the alkaline metals presents more difficulties than that of the corresponding compounds of ruthenium and rhodium. The double insoluble iridium and potassium salt is not remote from $(\text{IrO})_6\text{O}_3(\text{OK})_2$, which would be the potassium salt of a hexairidous acid. On operating at incipient redness in a muffle, the authors obtain a salt approximating to the formula $12\text{IrO}_2 \cdot \text{K}_2\text{O}$, the potassium salt of a dodeca-iridous acid.

On the Acid Ammonium Sodium Tungstates.—L. A. Hallopeau.—The author has obtained two salts, $16\text{WO}_3 \cdot 3\text{Na}_2\text{O}_3(\text{NH}_4)_2\text{O} + 22\text{H}_2\text{O}$, which loses 15 mols. of water at 100° ; and $12\text{WO}_3 \cdot 4\text{Na}_2\text{O}(\text{NH}_4)_2\text{O} + 25\text{H}_2\text{O}$, losing 19 mols. of water.

Rotatory Powers of some Amylic Derivatives in the State of Liquid and of Vapour.—Ph. A. Guye and A. P. do Amaral.—The results of the authors are given in the form of tables.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. x., No. 111.

New Process for the Purification of a large number of Organic Substances, Alimentary and Otherwise; in particular, Sugars, Alcohols, Potable Waters, &c.—E. Maumené.—The author's invention is the employment of a permanganate (potassium or calcium). The novelty of the process, as far as water is concerned, needs no discussion, since it is admitted in a foot-note that it is used by several London water companies.

Alloys of Iron and Chrome.—R. A. Hadfield.—(*Journal of the Iron and Steel Institute*). Abstracted by R. Masse.

Composition and Constitution of certain Alloys.—C. R. A. Wright.—From the *Journal of the Society of Chemical Industry*.

Progress of the Blast Furnace.—Paul Bayard.—It is here remarked that it is in Germany where the Thomas and Gilchrist process has made the most rapid and the most considerable progress. In 1883 it was under 500,000 tons, and has now reached 2½ millions.

MISCELLANEOUS.

Immunity against the Poison of the Cobra.—According to a paper read before the Royal Society of Edinburgh by Prof. T. R. Fraser, animals—man included—can be made non-susceptible to the venom of the cobra by the injection of minimal doses, gradually increased. He determined firstly the minimum dose fatal to rabbits, and then gradually increased the quantity until he reached an amount fifty times greater than the original fatal limit. A rabbit which he exhibited had thus received, in one hundred and fifty days, cobra poison enough to kill two horses! The effect on the general health of the subject was favourable; it had increased in weight from 2000 grms. to 3000; whilst its strength, and especially its virile power, was signally augmented. A successful antidote for the poison of the cobra is found to be a mixture of 3½ c.c. of the serum of a rabbit immunised up to thirty times the minimum fatal dose. We fear, however, that the shrieks of the zoöphilists will render this process useless in the British Empire.

NOTES AND QUERIES.

. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

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THE CHEMICAL NEWS.

VOL. LXXII., No. 1859.

NEW STUDIES ON THE FLUORESCENCE OF ARGON, AND ON ITS COMBINATION WITH THE ELEMENTS OF BENZENE.

By M. BERTHELOT.

I HAVE thought it useful to study in a more thorough manner the conditions of the combination of argon with benzene under the influence of the electric effluve, and those of the special fluorescence which accompanies it.

M. Deslandres, whose special competence in questions of photography is known to the Academy, has kindly lent me his assistance for these new determinations effected by means of stronger dispersions and defined by accurate photographs. It is my duty to express to him my thanks for this prolonged and difficult study.

We must remember that the combination of argon with the elements of benzene under the influence of the effluve is effected slowly; according to the present research it is effected with the co-operation of mercury, which intervenes in the state of a volatile compound. The use of discharges of great frequency does not appear to modify the general characters of the reaction.

At the outset we perceive nothing in diffused light; it is only in the dark room that we perceive a feeble violet light, similar in its intensity to that which the effluve generally develops in gaseous systems. After the lapse of an hour in the dark room we see a green light appearing, which occupies the middle of the interval between the spirals of the band of platinum coiled around the effluve tube; the luminous spectrum presents two yellow rays, 579 and 577 (in wave-lengths), a green ray, 546, and a green band, λ 516.5. These various rays will be defined presently.

The photographic spectrum now taken, with an hour's exposure, shows the principal bands of nitrogen, as well as a blue ray, 436, a violet ray, 405, and an ultra-violet ray, 354; these latter are fainter than the bands of nitrogen.

During the successive hours the green light augments without ceasing, the yellow rays and the ray 546 increase, and the band 516.5 diminishes. After eight hours the bands of nitrogen have almost disappeared in the photographs, doubtless because the corresponding nitrogen has been absorbed by the benzene.

Several further hours of effluve bring the fluorescence to a brilliant emerald light, visible in full daylight: the intensity of this phenomenon is not comparable with the fluorescence developed by the effluve in any known gas. The yellow and green rays may be seen and defined by spectroscopic in full daylight.

The photographs have shown the rays 579, 577, and 546; 436, 405, 354, 313, and 312 (ultra-violet). We perceive, further, two violet rays, 420 and 416, scarcely visible, and the rays 385 and 358.

The spectrum observed at the end of fifteen hours remained constant during thirty consecutive hours.

Although we have had recourse to photography to register these phenomena, we must not confound such effects observable in full daylight, and at a normal pressure, with the lights developed by the effluve on highly rarefied gases, such as are commonly observed with the spectroscopic.

This is the signification of these rays:—

The ray 579 is precisely one of the rays visible in full daylight, and at normal pressure which I have mentioned (*Comptes Rendus*, cxx., p. 800), indicating its probable fission. We must approximate to it the rays 580.1 and

577.1, mentioned in the spectrum of rarefied argon by Mr. Crookes (Jan. 24, 1895). The ray 546 has also been indicated (547) in my former paper, and corresponds to a strong ray, 545.6, exhibited by Mr. Crookes to the spectrum of rarefied argon. M. Deslandres has recognised these same rays in the spectrum of a specimen of rarefied argon which he had prepared by means of lithium. I have verified, by juxtaposition, the coincidence of the latter ray of rarefied argon with that of my effluve-tube. I have also pointed out the ray 436, found in the photograph, and very near to the 434.5 of the rarefied argon by Crookes. The rays 420 and 416 coincide with the very strong rays 420.1—419.8 and 415.96 of the rarefied argon of Crookes. The ray 405 may be identified with the ray 404.4 of Crookes (argon); I have verified the coincidence. The ray 385 coincides with a strong ray 385.15 of Crookes (argon); the ray 354 with a group of 354.7—353.4 of strong rays of rarefied argon (Crookes), and the ray 358 with a group of strong rays 358.7—357.5, observed by Crookes (in argon); λ 516.5 is a band of rarefied hydrocarbons; 313 and 312 are rays of the rarefied vapour of mercury.

None of these rays, as I have already remarked, coincides either with the ray of helium (587.5) or the principal ray of the aurora borealis (557), though this latter falls very near to a strong ray of argon (555.7). If the present fluorescence is not the same as that of the aurora, yet its development and the approximation of the rays above mentioned establish a probable relation between this meteor and the occurrence of argon in the atmosphere.

There appears here a very important circumstance. Already, on examining the table of the rays of rarefied argon given by Mr. Crookes, we recognise that certain of these rays coincide with certain of the rays of the rarefied vapour of mercury. The same coincidence is observed also in the finest rays visible in full daylight, at the normal pressure, in the fluorescence developed during the reaction of benzene upon argon. Such are, according to M. Deslandres, the yellow rays 579 and 577; such is the characteristic green ray 546; such are the blue ray 436, the violet ray 405, and the ultra-violet ray 354. On the contrary, the rays 420, 416, 385, and 358, belong only to argon, and the rays 313 and 312 to mercury.

M. Deslandres attributes the presence of the common rays to the presence of the vapour of mercury either in the rarefied argon or in the fluorescent light obtained with benzene at a normal pressure.

Nevertheless, as no known gas furnishes either this fluorescence or these rays, under the normal pressure, when operating over mercury, it is not possible to explain its formation by the mere presence of this vapour. Otherwise we could not comprehend why they do not equally originate with pure argon in presence of mercury at the normal pressure, and why they are not produced at the first moments of the effluve neither with argon saturated with benzene or carbon disulphide over mercury, nor with nitrogen under the same conditions in which it combines with benzene and carbon disulphide. On the contrary, with argon saturated with benzene they are developed only after the lapse of several hours, and consequently of the progressive transformation of the benzene into one of a series of compounds more and more condensed. It is one of these compounds which, at the moment of its formation, commences to unite simultaneously with argon and mercury, associated possibly in virtue of their common character of monatomic molecules. The fluorescence begins whilst there still exists in the tubes a considerable proportion of liquid benzene; it is then accompanied by a decrease of the gaseous volume.

This fluorescence subsists for a very long time, even after the benzene is no longer perceptible; finally the fluorescence ceases to manifest itself in full daylight, in consequence of the very prolonged action of the effluve, which at length causes the green tint to disappear, and brings back this gaseous system to a luminosity like that of ordinary gases. This happens doubtless in consequence

of the total destruction of the last traces of benzene and of the intermediate condensation products, which would maintain the equilibrium of dissociation of the system.

When once the green fluorescence is well established, the compounds which develop it are stable, *par se*; for it suffices, even after twelve hours of rest, without having disarranged the apparatus to cause the effluve to act anew, to re-establish the fluorescence, in all its splendour, in less than a minute. It is, however, extinguished immediately as soon as the electric action is suspended.

But if we separate the gas from the condensed matter, the phenomenon can be no longer reproduced immediately either upon the one or the other. The gas alone, if submitted to the action of the effluve, acquires almost immediately a peculiar violet fluorescence, visible in the dark, and which precedes the development of the beautiful green fluorescence. Still this is not then reproduced, which seems to indicate that the condensed matter may contain one of the products necessary for the equilibrium. If, on the other hand, we re-introduce fresh argon into the tube containing the condensed matter (free from visible benzene) the green fluorescence is not reproduced in its totality, but at the end of some time we see appear near the surface of the mercury, there where the rain of fire is most intense, a localised green tint which presents specific rays, though in a manner not very distinct. Their appearance is due, no doubt, to the existence (or the regeneration) of a trace of benzene, more or less modified. In fact, if we then introduce a few drops of liquid benzene into the tube containing the condensed matter and the fresh argon over the mercury, the action of the effluve for half an hour is sufficient to cause the green tint to re-appear in full splendour. But if there is an excess of benzene the phenomenon requires several hours for its re appearance.

These various observations, in conjunction with the limited character of the absorption of argon, show the existence of a complex equilibrium in which there intervene at once argon, mercury, and the elements of benzene, or rather a condensed compound derived from them.—*Comptes Rendus*, cxx., p. 1386.

ON ARGON.

By D. MENDELEEFF.

Is argon a chemical individual or a mixture? is it a simple or a complex body? Mendeleeff replies as follows:—The assumption that argon is a mixture appears quite improbable, as is especially shown by the experiments of Olszewski. The assumption of the composite character of argon has also little probability, though its exceptional stability is to a certain extent characteristic of some compounds. If we accept argon as an element, and further assume that its molecular weight is = 40, we must discuss a series of suppositions as to the atomic weight of this substance, which will evidently depend on the number of atoms in the molecule of argon corresponding to the series $A, A_2, A_3, \dots A_n$. To the first case there would correspond an atomic weight of about 40, when argon would appear as a monatomic element and as an analogue of Cd and Hg. For this view we have the relation K of the specific heats, which for argon has been found = 1.66. We must, however, consider that for the biatomic molecule of chlorine $K = 1.3$ instead of 1.4. If so active an element as chlorine possesses a smaller K , the extremely inactive argon must have a greater K , although its mol. consists of two or more atoms. For the atomic weight $A = 40$ there is no corresponding place in the periodic system. If the density of argon is below 20, it would come, according to its atomic weight, between chlorine and potassium, and must find its place in the eighth group of the third series; though in this series the existence of the eighth group is scarcely

admissible. Hence the assumption of an atomic weight $A = 40$ is scarcely probable.

To the second supposition, A_2 , there corresponds an atomic weight = 20, and argon must be introduced into the eighth group of the second series, *i. e.*, immediately after fluorine and before sodium, which is also not too probable, though more so than the case $A = 40$. If we accept A_3 , and if its atomic weight is consequently about 14, argon would appear as a condensed nitrogen, N_3 . In favour of this view speaks the common existence of argon and nitrogen in Nature; many lines of their spectra fall very near to each other, and the inert character of argon is intelligible if formed from N_2 with liberation of heat, and lastly, its formation from chemical nitrogen. This hypothesis, that $A = N_3$, might be tested by the introduction of boron or titanium into an atmosphere of argon through which electric sparks are caused to strike, and with strong heating.

If we assume A_4 or A_5 the atomic weight of argon would be = 10 or 8, and it would find no place in the periodic system. If we finally accept A_6 , and assume 6 atoms in a mol. of argon, there results an atomic weight of about 6.5, and the element falls in the first series, probably in the fifth group.

Hence the two most probable assumptions are:—1. That argon is a polymer of nitrogen = N_3 . 2. That the argon molecule is hexatomic, of course admitting that it is a pure elementary substance.

A. Gorbow remarks that the chemical inertness of argon is possibly due to its absolute dryness, since its discoverers have always dried it with P_2O_5 . He is of opinion that argon is possibly a nitrogen compound, *e. g.*, nitrogen silicide.—*Russian Physico-Chemical Society*, 1895, pp. 17 to 20, and *Zeit. Anorg. Chemie*.

COMPARISON BETWEEN THE SPECTRA OF THE GAS OF CLÈVEITE AND OF THE SOLAR ATMOSPHERE.

By H. DESLANDRES.

THE great discovery, by Prof. Ramsay, of a method of obtaining the gas helium, previously recognised only in the sun's atmosphere, equally interests astronomers and chemists.

At the outset the gas of clèveite and the sun's atmosphere have been respectively identified merely by the yellow ray D_3 , which they emit strongly; still the last communication from Prof. Clève seems to indicate other common radiations. I have therefore resolved to compare carefully the two lights over the greatest possible extent of the spectrum.

A capillary spectral tube, closed with a plate of quartz, was prepared and arranged so as to receive the gases emitted by a small crystal of clèveite, first heated and then brought in contact with pure rectified sulphuric acid. The spectra of the tube were accurately taken down before heating, after heating, and after the action of the acid, so as to recognise the gases successively liberated and to eliminate alien lights.

Before heating, the spectral tube, the pressure on which was about $\frac{1}{10}$ m. m., showed some of the rays referred to argon; then on heating (to about 300°) there was a plentiful liberation of an oxygen compound of carbon, apparently derived from a dissociated compound; for when the heat was continued the interior pressure increased and diminished on allowing the tube to cool. The yellow ray D_3 appeared only when the sulphuric acid had been in contact with the clèveite, at the same time with other strong rays, luminous and ultra-violet.

The author has collocated in a table the strongest new rays with their intensities (from 1 to 10, 10 signifying the strongest), and, in a parallel column, the rays already in-

dictated by Prof. Clève. He remarks, in a note, that after the ray D_3 he has not detected the rays announced by Mr. Crookes. Opposite the above he has placed the nearest rays of the solar chromosphere, as determined by Mr. Young in the luminous region and by himself in the ultra-violet region. The intensities are represented with a scale of 1 to 100, and another column shows the frequency of these chromospheric rays, i.e., the number of times that they occurred in the atmosphere in 100 observations. The rays which occur always are thus followed by the number 100; they are called *permanent* rays. They are not numerous, as we find only 11 in the luminous region, 5 being due to hydrogen and 2 to calcium. The four others, among which is the ray D_3 , are not referred to known elements.

The gas of clèveite emits, therefore, besides the ray D_3 , several other strong rays of the chromosphere, and in particular the ray $447\cdot18$, which is permanent, so that the number of the sun's permanent rays not recognised upon the earth is reduced to two.

Lastly, other strong rays of clèveite, such as the green ray $\lambda 501\cdot60$ and the ultra-violet ray $\lambda 388\cdot8$, have in the sun's atmosphere neither the same relative intensity nor the same frequency as the ray D_3 ; thus we are led to think that the gas is a mixture or a compound.

I will mention two other facts in support of this opinion:—

The ray D_3 in the spectral tube is seen only in the capillary part and at the positive pole; it is wanting at the negative pole, whilst the green ray $\lambda 501$ is there very brilliant.

Lastly, Prof. Lockyer has found, in bröggerite, a mineral closely allied to clèveite, only a part of the foregoing rays.—*Comptes Rendus*, cxx., p. 1112.

DETERMINATION OF SULPHUR IN CAST-METAL, IN STEELS, AND IRON.

By LOUIS CAMPREDON.

Principles of the Method.

1. LIBERATION of the sulphur in the form of gaseous compounds, by attacking the metal with dilute hydrochloric and sulphuric acids.

2. Passage of the gases, with the addition of carbonic acid and hydrogen, into a tube of porcelain heated to redness, according to the indications of Rollet to transform the sulphurous compounds disengaged into hydrogen sulphide.

3. Causing the gas to bubble through a slightly acid solution of zinc acetate, to retain the hydrogen sulphide in the state of zinc sulphide insoluble in weak acetic acid.

4. Sulphydrometric titration of the zinc sulphide formed by means of a standard solution of iodine and a solution of sodium thiosulphate, to determine the quantity of iodine present in excess. The end of the reaction is marked by the very distinct disappearance of the blue colour of the solution in presence of starch (added as indicator), when no trace of free iodine remains.

The zinc sulphide formed, submitted to the action of an excess of iodine, gives $ZnS + I = ZnI + S$.

This reaction, the exactitude of which has been verified, is effected in a neutral liquid or in an acid liquid without action upon the zinc sulphide.

Description of the Apparatus.

It includes two continuous appliances for the production of carbonic acid and hydrogen. These gases pass into a solution of silver nitrate, to hold back the sulphuretted compounds which they may contain; they then arrive in the solution flask, where they mix with the gaseous products resulting from the action of the acid employed upon the metal. The gases are cooled by their

passage into a condensing flask immersed in water, and which retains the greater part of the watery vapour. The gaseous mixture then traverses a tube of porcelain heated to orange redness or to incipient whiteness, and bubble into a Durand flask containing 100 c.c. of solution of zinc acetate, prepared according to the directions given below. Finally, the gases traverse a solution of lead acetate (slightly acidified with nitric acid), which must not be rendered turbid by the passage of the gaseous current, thus proving that all the hydrogen sulphide has been kept back.

Method of Manipulation.

We operate upon 2, 5, or 10 grs. of the metal, according to its supposed proportion of sulphur.

The apparatus having been fitted up, as shown above (the current of carbonic acid being established and that of hydrogen arrested), we introduce the metal in fine filings into the solution flask, taking all the due proportions to avoid the formation of an explosive mixture, for which purpose it is sufficient to maintain in the tube, at the beginning of the operation, an atmosphere of carbonic acid.

The stopper of the solution flask is inserted, and we introduce, by means of a tube-funnel fitted with a cock, 100 c.c. of sulphuric acid at 1:5, or of hydrochloric acid at 1:3. The action is kept up in the cold for two or three minutes, still maintaining the stream of carbonic acid; heat is then applied, and the current of hydrogen is allowed to enter.

In the first Durand flask there is formed a white flocculent precipitate of zinc sulphide.

When the reaction is completed we remove the conical solution flask, as also the first Durand flask containing the zinc sulphide. The tubulures are washed by means of a jet from the washing-bottle, to remove any adhering portions of sulphide, and we separate the tubulure. The titration is effected in the Durand flask itself, so as to dispense with any transfer of the precipitate.

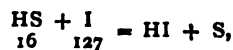
We add, from a burette, a known quantity of iodine, more than sufficient to decompose the zinc sulphide according to the equation indicated above; we leave the reagents in contact for two or three minutes, stirring the mixture, and then add 2 c.c. of liquid starch-paste, which produces a greenish colouration. We then run into the flask from a burette, stirring the liquid gently, sodium thiosulphate, until the colouration—which was at first deep green and then indigo-blue—disappears entirely. The iodine acting upon the sodium thiosulphate in presence of water produces sodium tetrathionate and hydriodic acid.

Preparation of the Solutions.

1. *Zinc Acetic Solution*.—Dissolve 10 grms. pure zinc oxide in 25 c.c. of crystallisable acetic acid, dilute to about half a litre, add an excess of ammonia until the precipitate of oxide formed re-dissolves, and then render it slightly acid with acetic acid.

2. *Solution of Iodine*.—Dissolve 7·9 grms. of triply sublimed iodine and 25 grms. potassium iodine in 1 litre of water.

According to the formula of the reaction—



we see that—

$$\frac{127}{16} = \frac{7\cdot9}{1},$$

so that 7·9 grms. of iodine correspond to 1 gm. of sulphur.

3. *Starch Liquor*.—Take 1 gm. of wheat starch, pulverise in a mortar, add a little water to obtain a thin paste, which is poured into a beaker of Bohemian glass containing 150 c.c. of boiling water; let settle, and decant the clear liquid.

Fresh starch liquor ought to be prepared daily.

4. *Solution of Sodium Thiosulphate*.—Dissolve 10 grms. thiosulphate in water, adding 2 grms. ammonium carbonate and water enough to make up 1 litre. The ammonium carbonate increases the stability of the thiosulphate.

The iodine and the thiosulphate solutions are preserved in the dark in bottles of yellow glass.

Conclusion.

The process just described is very expeditious; the sulphur is determined in thirty minutes at most. For cast metal the action must be prolonged a little, to make sure that it is complete. This we ascertain by changing the first Durand flask, and substituting a second one containing a clear solution of zinc acetate. If in this second flask there is produced a precipitate of zinc sulphide, it is titrated like the former.—*Comptes Rendus*, cxx., 1051.

ON A NEW FORM OF CHEMICAL BALANCE.

By H. JOSHUA PHILLIPS, F.I.C., F.C.S.

THE writer has recently been experimenting with hydrometers, to ascertain to what extent they could be applied to act as a chemical balance; the result of which was, after several trials, the making of an instrument which for certain purposes will be found to be useful. The following is a sketch and description of the instrument:—



It consists of a glass cylinder upon the top of which can be fixed a portable brass ring containing two upright guide-rods of brass, 6 inches high and $\frac{1}{2}$ inch in diameter. The balance proper consists of gilded brass bulbs into which is screwed an aluminium stem. Screwed on to the top of the stem there are arms, also of aluminium, which are perforated at each end so that the guide-rods can pass through them. Upon the centre of the arms there is a receptacle for a small aluminium scoop or pan to hold the substance to be weighed. Underneath the arms it will be seen there are projecting needle-points; there is also a movable point upon one of the guide-rods. The manner of using the instrument is as follows:—The cylinder is first filled with cold recently-boiled water; the bulbs and attachments are then dropped in, the guide-rods passing through the perforations of the arms. The balance sinks into the water until the bulbs are just covered. Supposing 0.2 grm. of steel drillings are desired to be weighed. A 0.2 grm. weight is dropped into the portable pan; the bulbs then sink to a definite depth, and which can be ascertained by bringing the movable needle-point upon the guide-rod so as to face the point fixed upon the arm. The weight is now taken off, and the bulbs rise again. The sample of steel drillings is now gradually introduced into the empty pan until the needle-points are again opposite each other,—gently tapping the

instrument to remove any friction,—and the 0.2 grm. of steel is thus quickly obtained. The range of weight that such an instrument is capable of recording must of necessity be of narrow limits. The depth to which the instrument will sink in the liquid with a given weight, and also its delicacy, will depend upon the diameter of the stem. The diameter of the stem of the balance shown in the sketch is $\frac{1}{8}$ inch, and a load of 0.2 grm. will sink it about $3\frac{1}{2}$ inches. The height of the cylinder is 10 inches, and its diameter $1\frac{1}{2}$ inches, and the total length of the stem $5\frac{1}{2}$ inches. An instrument of these dimensions will be found useful for weighing steel for carbon tests, &c., and also for weighing certain precipitates, &c. The sole makers are Messrs. Townson and Mercer, of 89, Bishopsgate Street, London, E.C.

Palace Chambers, Westminster, S.W.

CHEMISTRY OF THE LIGNOCELLULOSES: A NEW TYPE.

By W. C. HANCOCK and O. W. DAHL.

THE pith-like stem of *Aeschynomene Aspera** offers a very exceptional instance of wood formation. Although, from considerations of external resemblance, it is often described as a *pith*, its morphological characteristics are those of a true wood (De Bary, "Comparative Anatomy of the Phanerogams," p. 499). The reactions of this wood-substance, on the other hand, show important exceptions from those characteristics of the lignocelluloses. Solutions of aniline salts and of phloroglucol in HCl give the faintest colouration only with the main mass of the cellular tissue, reacting strongly with only a few cells situate near the central axis, and certain vessels disposed at intervals and concentrically in the radial line of cells.

In this preliminary microscopical examination our results were confirmed by competent botanists, who described this wood as consisting in the main of cellulosic tissue, with a small proportion of lignified elements disposed as described.

Having submitted the material to exhaustive chemical investigation on the lines laid down by Cross and Bevan ("Cellulose," p. 94), we find it to be a lignocellulose of normal constitution. Those reactions and decompositions which are related to constitution are identically those of the typical members of the group. But these typical characteristics are associated with divergence in minor points, and particularly in regard to the absence of those constituents upon which the colour-reactions in question depend. It has previously been shown (Cross and Bevan, *Chem. Soc. Trans.*, 1883, p. 18) that the yellow reaction with aniline sulphate is a reaction of an aldehydic or quinonic by-product. Thus the jute-fibre substance, after boiling in a solution of sulphite of soda, or when re-precipitated from solution in ZnCl_2 -Aq, no longer reacts with aniline salts.

Similarly the phloroglucol reaction is that characteristic of pentosanes, and is no doubt due to their presence in the majority of lignocelluloses. In the particular instance of *Aeschynomene* we have a wood giving the large yield of furfural characteristic of the group, but the pentosan reaction only in scattered cells.

The wood of *Aeschynomene* affords, therefore, another and striking instance of furfural yielding constituents of tissues not pentosans (*comp. Ber.*, 1894, 1061).

The following are the results of experimental determinations of the more important reactions and constants.

Physical Characteristics.

The cylindrical stems are made up chiefly of thin-

* The plant is one of the Leguminosae, of aquatic habit, the wood being modified to serve as a float. The product has extensive industrial uses, e.g., in the manufacture of pith helmets. See "Dictionary of Economic Products of India," Watt, vi., p. 125.

washed, air-filled cells; 1 grm. of the substance having the enormous volume of 45 to 50 c.c.

The substance in its natural form appears opaque white; on compressing to denser masses it is seen to have a yellowish colour.

Reactions.

With solution of aniline salt a faint yellow, giving the reaction of the lignocelluloses only in isolated cells. With phloroglucol and HCl, a faint pink; the full red colouration characteristic of the lignocelluloses (pentosane constituents) in isolated cells only, as with the preceding reagent.

With Schulze's solution (I in KI + ZnCl₂) a brown colouration, giving place to greenish-blue in washing.

With a solution of iodine in strong aqueous hydriodic acid (1·5 sp.gr.) it is stained a pure blue, not removed by washing.

The ordinary woods are stained purple-brown with this reagent, which is changed to brown on washing. In this reaction, therefore, there is a decided resemblance to the celluloses.

With the aniline colours the tissue is dyed in most cases uniformly. So also with ferric ferricyanide (*infra*). In this reaction the tissue shows the distinctive characteristics of the lignocellulose group.

The tissue, unlike the majority of lignocelluloses, does not reduce Fehling's solution on boiling.

Composition.

In the air-dry condition the substance retains only 8·6 per cent moisture. The mineral constituents amount to 1·9 per cent.

Elementary Analysis.—The following results were obtained, calculated in the dry ash-free substance:—

C	46·9	46·2
H	7·1	6·4

These numbers are approximately those of the jute fibre substance.

Alkaline Hydrolysis.—On boiling with alkaline solutions (1 per cent NaOH) the substance rapidly loses 29·0 per cent of its weight. On prolonged boiling (60 minutes) the further action of the alkali is only slight, the total loss of weight being 29·8 per cent.

Cellulose.—After boiling with alkaline solutions as above, and washing, the substance gives with chlorine the ordinary reaction of lignocelluloses, forming a yellow quinone chloride, dissolved by sodium sulphite (sol.) to a deeply coloured solution. The cellulose isolated by this treatment amounted to 54·4 per cent.

Constants of Chlorination.

Determinations were made of the volume of chlorine absorbed in the above reaction, and of the hydrochloric acid formed; the quantities being calculated to the reduced weight of the product, i. e., the weight after boiling with the alkaline solution (Cross and Bevan, *Chem. Soc.*, 55, 199).

(a.) Weight of wood, 1·24 grms.; reduced weight, 0·966 grm.

Conditions: Moist Cl gas at 21·5° and 760 m.m.

Time in minutes: 0 5 10 15 20 25 40 50 60 210.

C.c. gas absorbed: 0·44 55 60 64 66 70 72 79 94.

Total absorption calculated to chlorine at 0°, 760 m.m.—84·5 c.c.

(b.) Weight of substance, 2·062 grms.; reduced weight, 1·610 grms.

Conditions: Moist Cl gas at 19·5° and 766 m.m.

Time in minutes: 0·5 10 15 20 25 30 35 40 50 60.

C.c. gas absorbed: 0·71 79 86 91 95 97 98 99 102 106.

Total absorption calculated to Cl at 0°, 760 m.m.—93·3 c.c.

The main reaction reaches its limit after about thirty minutes' exposure; the subsequent exposure is due to

secondary reactions, attended by decompositions of the chlorinated derivatives.

This conclusion is confirmed by the following determinations:—

	(a.)	(b.)
Chlorine as HCl formed in the reaction	0·1526 grm.	0·1278 grm.
Chlorine in combination with wood constituents	0·0750	0·1633
Total chlorine	0·2276	0·2911
Total Cl estimated by absorption	0·2782	0·2964

It is evident that the abnormal figures of experiment (a) are due to the prolonged exposure of the substance to the halogen.

Taking the figures for the total absorption after thirty minutes' exposure to the gas, when the main reaction may be regarded as completed, they are, calculated on the weight of the lignocellulose taken: in (a) 20 per cent, in (b) 16 per cent; mean 18·55 per cent.

The combined chlorine estimated in (b), also calculated on the lignocellulose, is 10 per cent. This reaction, therefore, is shown to be that generally characteristic of the lignocelluloses; the quantitative results being intermediate between those obtained for the jute fibre, on the one hand, and the woods on the other ("Cellulose," p. 180).

Furfural.

The furfural constants, determined by the method of Flint and Tollens (*Landw. Vers. Stat.*, xlii., 381). The furfural was estimated in the entire wood substance, and also in the products of the alkaline hydrolysis. Results were as follows:—

	Furfural.
Whole wood substance	11·6 p.c.
Products of alkaline hydrolysis, soluble ..	3·6
" " " insoluble ..	8·0

Of the total furfuroids, therefore, 69 per cent remain in the residue unattacked by the alkaline solution. As the proportion of residue is 70 per cent of the original wood (*supra*), it will be seen that the ratio to the other constituents, or, in short, the distribution of the furfuroids, is unaffected by the alkaline treatment. The furfuroids therefore are not present as pentosanes, or at least are in small proportion.

Methoxyl.

The substance was treated according to the method of Zeisel: OCH₃ estimated = 2·9 per cent, calculated on the dry ash-free substance. This number is considerably less than for the woods generally, and 20 per cent less than for jute. (See Benedikt and Bamberger, *Monatshft.*, ii., 260—267.)

Ferric Ferricyanide Reaction.

The reaction of the lignocelluloses with the solution, obtained by mixing ferric chloride with potassium ferricyanide in equivalent proportions, is a distinguishing characteristic; and the wood of *Aeschynomene* gives an equally pronounced reaction, being dyed evenly to the deepest colour with a very large increase of weight, due to the fixation of the ferroso-ferric cyanide. The following results were obtained:—

(a.) 1 grm. lignocellulose increased to 1·958 grms.
(b.) 1 " " " 1·747 "

the lignocellulose being boiled in water to expel air, and digested some hours with excess of solution of ferric-ferricyanide, obtained by mixing normal solution of Fe₂Cl₆ and K₃Fe(CN)₆ in equal volumes. The gain in weight, due to absorption of the blue cyanides, exceeds 100 per cent, calculated on the dry ash-free lignocellulose.

In the resulting products the Fe was determined as

Fe_2O_3 and the N as NH_3 , and the molecular ratio Fe : CN found to be 1 : 2.4. The blue cyanide fixed by the lignocellulose has the composition $\text{Fe}_5(\text{CN})_{12}$.

Nitrates.

The substance shows the usual reaction of the lignocelluloses with nitric acid in presence of sulphuric acid. It is coloured to a red-brown, which gives place to a bright yellow on washing. It gives low yields of nitrate (110 per cent), and in this respect is shown to be constitutionally more really related to the woods than to the fibrous lignocelluloses. The nitrates, moreover, contain a low proportion of O.N.O_2 groups, yielding on analysis N = 7–9 per cent—and are insoluble in the usual solvents of these compounds.

Thiocarbonate Reaction (*J. Chem. Soc.*, 1893, 837).

The lignocellulose yields to a certain extent to the joint action of the caustic alkalis and carbon disulphide, the reaction which ensues resembling that of the jute fibre.

The substance is gelatinised, but only a small proportion—20 to 30 per cent of its weight—passes into solution when treated with water. This affords additional evidence of the small proportion of free alcoholic OH groups.

By the foregoing results this peculiar product of growth is completely identified as a lignocellulose. To botanists this identification will have a special significance as presenting a type of lignification of unique characteristics. Regarded from the chemical point of view, the most important points established and confirmed are:—

1. The existence of a lignocellulose having the essential constitutional features of the group, but devoid of free aldehydic groups and characterised by colour reactions, which are only in part those of the lignocelluloses generally; in others showing a close resemblance to the celluloses.
2. Certain colour reactions, frequently regarded as essentially characteristic of the lignocelluloses proper, are in effect due to by-products.
3. Owing to the unusual conditions of growth, and metabolism obtaining in a tissue, specialised to serve an exceptional function, these by-products are not formed in a large proportion of the cells, which are nevertheless shown to consist of true lignocelluloses.
4. That the true lignocelluloses contain furfural-yielding constituents—furfuroids—which are not pentosans.

NOTE.—We are indebted to the authorities of the Imperial Institute for a liberal supply of the raw material.

Laboratory of Messrs. Cross and Bevan,
London, W.C.

A REVISION OF THE ATOMIC WEIGHT OF STRONTIUM.

FIRST PAPER: THE ANALYSIS OF STRONTIC BROMIDE.*

By THEODORE WILLIAM RICHARDS.

Earlier Work.

A GLANCE at published results shows that the atomic weight of strontium has not been investigated for thirty-five years. The early determinations, good enough for their time, show variations which render them quite unsatisfactory to-day; and the case is parallel in every respect to that of barium, which has formed the subject of two recent papers (*Proc. Amer. Acad.*, xxviii., 1; xxix., 55).

The oldest experiments of any note upon the atomic weight of strontium are those of Stromeyer (*Schweig. J.*,

xix., 228; Meyer u. K. Seubert's "Atomgewichte," p. 123), who measured, in 1816, the gas evolved from strontic carbonate upon its decomposition by an acid. The result, which is only of interest historically, gives $\text{Sr} = 87.3$, if a litre of carbon dioxide weighs 1.977 grms. under normal conditions.

At about the same time Rose (*Poggendorff's Annalen*, viii., 189) found that 181.25 parts of argentic chloride could be obtained from 100 parts of strontic chloride,—data which indicated $\text{Sr} = 87.31$. Twenty-seven years afterward, in 1843, Salvétat (*Comptes Rendus*, xvii., 318) determined by loss of weight the carbon dioxide in strontic carbonate, and concluded that the metal must be 88.0,—a result which scarcely improved the situation.

Subsequently, in 1845, Pelouze (*Ibid.*, xx., 1047) found the amount of silver necessary to precipitate a weighed amount of ignited strontic chloride; his results give the value $\text{Sr} = 87.70$. Thirteen years later Marignac (*Liebig's Annalen*, cvi., 168) repeated these experiments, determining also the amount of crystal water in crystallised strontic chloride, as well as the amount of strontic sulphate obtainable from the salt. Thus he found that 15,000 grms. of crystallised strontic chloride yielded 8,9164 grms. (corrected by L. Meyer u. K. Seubert, "Atomgewichte," pp. 78, 79) of the anhydrous salt and 10,3282 grms. of strontic sulphate; moreover, 15,000 grms. of hydrated strontic chloride required 12,1515 grms. of silver for precipitation. Another similar series of experiments upon the water of crystallisation made its amount appear 3 m.grms. more than before. These data give basis for a number of possible values for the atomic weight of strontium, ranging from 87.17 to 87.55, the individual figures being tabulated below.

In 1859 Dumas (*Liebig's Annalen*, cxiii., 34) published another determination of the ratio of strontic chloride to silver, the salt having been fused in a stream of hydrochloric acid. Altogether, 27,3435 grms. of strontic chloride required in his hands 37,252 grms. of silver, the individual values for strontium varying from 87.3 to 87.8. Since this time the subject has remained untouched.

Below is tabulated a list of the various determinations, grouped according to the ratios determined.

The Atomic Weight of Strontium.

Oxygen = 16.000.

From the carbonate:—

Stromeyer, 1816 87.30
Salvétat, 1843 88.00

Ratio of strontic and argentic chlorides:—

Rose, 1816? 87.31

Ratio of anhydrous strontic chloride to silver:—

Pelouze, 1845 87.70
Marignac, 1858 87.48
Dumas, 1859 87.53

Ratio of crystallised strontic chloride to silver:—

Marignac, 1858 87.52

From the crystal water in strontic chloride:—

Marignac, 1858 87.35

Ratio of anhydrous and crystallised strontic chloride to strontic sulphate:—

Marignac, 1858 87.2 to 87.6
Selected by Clarke 87.58
Selected by Meyer and Seubert 87.5
Selected by Ostwald* 87.5

A critical review of the list reveals a great lack of trustworthiness in all the figures. The values deduced from the carbonate, and those involving water of crystallisation, may all be thrown out at once; and the results yielded by the displacement of hydrochloric by sulphuric acid are but little better. The series upon which most

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy*.

* Much assistance in preparing this list has been obtained from the well-known works of these authors. The figures have all been based upon the most recently accepted atomic weights.

chemists have relied—the one based on the titration of the chloride by means of silver—is hopelessly vitiated by the imperfect execution of the method of analysis (*Proc. Amer. Acad.*, xxix., 80 *et seq.*). If any further proof of this uncertainty were needed, the following table, giving a comparison of the work of different experimenters upon other chlorides, would furnish it:—

Molecular Weight of Chlorides by the Method of Gay-Lussac.

	Pelouze.	Marignac.	Dumas.	Stas.	
				1st.	2nd.
NaCl ..	58.434	—	58.468	58.506	58.503
KCl ..	—	74.539	—	74.583	74.600
NH ₄ Cl ..	53.464	53.450	—	53.530	53.532

Thus Pelouze, Marignac, and Dumas all obtained low results with the method of Gay-Lussac; in fact, the error sometimes exceeded the tenth of 1 per cent. The cause of this error, which appeared also in the work of these experimenters upon barium, has already been pointed out in another paper (*Proc. Amer. Acad.*, xxxix., 80.).

We are thus led to infer that the true molecular weight of strontic chloride must exceed the usually accepted value, 158.4, by about one-tenth of 1 per cent, and that the true atomic weight of strontium must be nearly 87.7. This inference is confirmed by the result of the investigation now to be described.

The balance and weights, and the methods of weighing and of tabulating results employed in the work recounted below have already been described in sufficient detail (*Proc. Amer. Acad.*, xvi., 242; also xxviii., 5). The balance seems to have increased slightly in sensitiveness during its four years' work, owing perhaps to the smoothing of microscopic roughnesses in the bearings. It is almost needless to say again that the weights were carefully standardised from time to time, and the small, surprisingly constant corrections were always applied. The correction to the vacuum standard was calculated by the usual formula:—

$$\left(\frac{0.001293}{\text{sp. gr. substance}} - 0.000156 \right) \frac{H}{760} \frac{273^\circ}{273^\circ + t^\circ}$$

= correction in grms. for 1 grm. of substance.*

The values thus calculated for the appropriate substances at 20° and 760 m.m., were as follows:—

Correction to be Applied to One Grm. of Substance.

Silver	−0.000031 grm.
Argentio bromide	+0.000043 ..
Strontic bromide	+0.000141 ..

The general plan of the following work was similar to that adopted in the case of barium. For obvious reasons the bromide of strontium was chosen as the starting-point; and the investigation began with a study of the properties of the salt, in order to determine its fitness for the purpose.

The atomic weight of silver is assumed to be 107.93, and that of bromine 79.955, unless a definite statement to the contrary is made.

Properties of Strontic Bromide.

The properties of the bromide of strontium resemble very closely those of the corresponding salt of barium. As is well known, however, the strontium salt usually crystallises with six instead of with two molecules of water. The crystals, unlike those of the barium salt, are

noticeably hygroscopic in ordinary air, so that they cannot be weighed with great accuracy; they melt easily in their own water of crystallisation at about 100°. This water fact renders more difficult the quantitative drying

upon a watch glass. H = atmospheric pressure; t° = atmospheric temperature at the time of weighing; 0.000156 = standard weight of air displaced by 1 grm. of brass.

of the salts; indeed, in the few cases where the water of crystallisation was determined, it was necessary to allow the crystals slowly to lose their water in a desiccator before ignition. Thus it was found in the following experiment that five molecules of water were given off, the sixth having very little, if any, tension at ordinary temperatures.

	Grms.
Initial weight of strontic bromide	1.3305
Constant weight after three weeks over	
H ₂ SO ₄	0.9926
Heated to 200° for three hours	0.9246
Loss of weight in dry air, found	25.41
" " " calc. for 5H ₂ O	25.33
Additional loss on ignition, found	5.11
" " " calc.	5.06

A week's standing in the air of the laboratory sufficed to supply again all the water which had been lost. These results point without doubt to the existence of a definite substance having the formula SrBr₂.H₂O, which is hygroscopic in the air and corresponds to the compound BaBr₂.H₂O, obtained in a similar way (*Proc. Am. Acad.*, xxviii., 12, footnote). The existence of this substance has already been inferred by Lescaeur (*An. de Chim. et de Phys.*, [6], xix., 553, 1890) from observations of the vapour tension of the crystal water. Anhydrous strontic bromide is perhaps even more hygroscopic than the corresponding salt of barium.

Strontic bromide melts to a transparent liquid at 630° (Carnelley), losing bromine in noticeable quantities if exposed to the air for some time at this temperature. Fused in a current of dry hydrobromic acid the salt soon recovers this lost bromine, and upon subsequent solution in water shows itself to be wholly neutral both to phenolphthalein and to methyl orange. It will be seen that this fact is of the utmost significance. The cold fused transparent or translucent mass is much less hygroscopic than the powder from which it was made.

The importance of driving out every trace of water from the salt before weighing cannot be over-estimated. Systematic experiments (*Proc. Amer. Acad.*, xxviii., 12; xxix., 58) with baric bromide and chloride led to the conclusion that probably neither of these salts retains water at a red-heat, and it was to be expected that the same fact might be true of the substance in hand. In order to test the point, 4 grms. of very pure strontic bromide dried at about 400° were fused in a stream of hydrogen bromide. The mass gained nearly 6 m.grms. in weight, showing that the loss of bromine in the air at 400° much more than counterbalanced a possible trace of water. Again, 11.2610 grms. of the same specimen, dried at 305° until constant in weight, were found to weigh 11.2630 grms. after fusion as before. Since these gains corresponded closely with losses of bromine found alkalimetrically in similarly heated but unfused samples, it is evident that very little if any water can be held by the dried salt. It has already been pointed out that no absolute proof of such a fact is possible (*Proc. Amer. Acad.*, xxviii., 14); and these experiments, together with the analogy furnished by the more manageable barium salts, seem to be the last resort. The apparatus used for these experiments will be described under the heading "Method of Analysis."

The specific gravity of anhydrous strontic bromide has been found by Bödeker to be 3.96. Since no more recent data regarding this constant could be found, another determination, described below, seemed to be needed. 3.2560 grms. of a pure specimen which had been fused in the air and dried at 200° in the pycnometer were found to displace 0.6678 grm. of toluol at 24°. Since the specific gravity of the toluol under these conditions, referred to water at 4°, was found to be 0.8618, that of the strontic bromide referred to the same standard must be 4.203. Again, 2.3065 grms. of strontic bromide which had been used in a stream of hydrobromic acid displaced 0.4699 grm. of toluol, thus having a specific gravity of 4.229.

The mean of these determinations, 4.216, was adopted as the basis of the reduction of the weighings to the vacuum standard.

Strontic bromide, like baric bromide and chloride, may be evaporated to apparent dryness over a free flame in a platinum dish without losing a trace of halogen. Experiment showed that, upon mixing pure bromide of strontium with small quantities of bromide of calcium and barium and crystallising the mixture, both impurities tended toward the mother liquors. Hence simple crystallisation affords a method of eliminating the two most likely impurities.

The other properties of strontic bromide do not pertain especially to the present work.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, June 28th, 1895.

Dr. GLADSTONE, Vice-President, in the Chair.

Mr. BOWDEN read a note on "*An Electro-Magnetic Effect.*"

A long glass tube containing mercury, and fitted with a small stand-pipe to indicate the hydrostatic pressure, is passed between the poles of an electro-magnet. On passing a current of about 30 amperes through the mercury in this tube, the stand-pipe being turned so as to indicate the pressure either perpendicular or parallel to the lines of force of the field of the electro-magnet, movements of the mercury in the stand-pipe take place. When the stand-pipe is perpendicular to the lines of force of the field, the mercury rises or falls according to the direction of the current. When the stand-pipe, however, is parallel to the lines of force, the mercury always rises whatever the direction of the current.

Prof. S. P. THOMPSON said there appeared to be three unexplained effects—one proportional to the current and the field, and reversible; another, independent of the direction of the current or of the field; and a third, which only occurred while the current was changing in strength. In addition there may be a fourth effect, which up to now has not been noticed. The motion of the mercury column in Fig. 1 was in the opposite direction to that of the drag on a conductor carrying the current. An apparent rise in pressure might be due to a decrease in the density of the mercury due to the heat developed by the current.

Mr. BLAKESLEY asked if the author had noticed any changes in level in the mercury reservoirs at the ends of the tube.

The author, in his reply, said the reservoirs at the ends were so large that no changes of level were appreciable.

Mr. RHODES read a paper on "*The Armature Reaction on a Single Phase Alternating Current Machine.*"

In this paper the author gives the investigations that were the subject of a verbal addendum to a paper read before the Society on a previous occasion. He investigates the lag or lead of the E.M.F.'s over the current, and applies the results to examine whether the field excitation of the generator or the motor is strengthened or weakened by the reaction of the armature currents.

Mr. TUNZELMANN expressed a hope that the author would amplify parts of his paper.

Mr. BLAKESLEY said the conclusion of the author, that "either of two alternate current machines may be driven as a motor by the other, irrespective of their relative E.M.F.'s," is not invariably correct. The facts of the case were these:—The E.M.F. of the motor may exceed that

of the other machine to a certain extent; but that E.M.F. multiplied by the cosine of the angle of electric lag must yield a product not greater than the E.M.F. of the generator,—i. e., using Mr. Rhodes's symbols, $\epsilon \cos \theta$ must not be greater than E. Mr. Blakesley gave a geometrical proof of this; but the same proposition had been given by him some ten years ago, in the course of investigating the subject generally. This was at a time when Dr. John Hopkinson was, with less than his usual perspicuity, teaching that synchronous alternate current machines could not be run in series with stability, both doing work. Referring to the author's diagrams, Mr. Blakesley said that in a problem involving so many elements as that under consideration, it was impossible, with the limited dimensions of space, to represent the results with the complete generality of a formula. Some elements had to be taken as the independent, others as the dependent, variables. The author had considered the power transmitted to the motor, the E.M.F. of the generator, and the angle of electric lag, as independent; the E.M.F. of the motor as dependent. In Mr. Blakesley's original diagrams the E.M.F.'s were both considered independent, as well as the electric lag, and the powers applied or transmitted as dependent variables. In any case the formulæ properly derived from such diagrams became perfectly general, and it did not appear to him that the change of method indicated could properly be called a new theory on the subject. As a matter of fact, diagrams based on the independence of the E.M.F.'s and the electric lag would furnish a better means of discussing the question of the stability of the motion than Mr. Rhodes's plan, and this might account for the entire omission from the paper of this important matter.

Prof. S. P. THOMPSON said it was impossible to discuss the question of stability till the subject of armature reaction had been thoroughly investigated. The terms lag and lead had been used by Mr. Rhodes in a constant manner; but this was not always done, and he recommended that the phase of the current which was common to both generator and motor be taken as the standard.

The author, in his reply, said he agreed with Mr. Blakesley that there was a limit to the extent to which the motor might be excited, and this upper limit could easily be obtained from the figure given in the paper. The question of armature reaction was, however, most important, as it might excite the field two or three times more than the original excitation. Since motors were designed to do a certain amount of work, and not the work to fit the motor, it was most natural to take the output of the motor as fixed.

Mr. SHELFORD BIDWELL read a paper on "*The Electrical Properties of Selenium.*"

The author has continued his investigations on this subject, and has come to the following conclusions:—(1). The conductivity of crystalline Se appears to depend principally on the impurities which it contains in the form of metallic selenides. It may be that the selenides conduct electrolytically, and that the influence of light in increasing the conductivity is to be attributed to its property of facilitating the combination of Se with metals in contact with it. (2). A Se cell having platinum electrodes and made with Se to which about 3 per cent of cuprous selenide has been added, is, even though unannealed, greatly superior both in conductivity and sensitiveness to a similar cell made with ordinary Se and annealed for several hours. (3). Red Se in contact with copper or brass is quickly darkened by the action of light, owing, it is suggested, to the formation of a selenide. (4). Crystalline Se is porous, and absorbs moisture from the air, and it is this moisture that causes the polarisation of Se after the passage of a current. (5). The presence of moisture is not essential to sensitiveness, but appears to be in a slight degree favourable to it. (6). If cuprous selenide is made the kathode in an electrolytic cell, and a strip of platinum the anode in water, red Se mixed with

detached particles of the selenide is deposited in the water. (7). The photo-electric currents sometimes set up when light falls upon Se are dependent upon the presence of moisture, and are no doubt of voltaic origin. (8). Perfectly dry Se is below platinum in the thermo-electric series.

Prof. MINCHIN (communicated) suggested that the selenium "cell," should be called a selenium "resistance." A grid having one terminal made of aluminium and the other of copper might form a true cell, and might generate an E.M.F. when light fell on it. He (Prof. Minchin) would like to know if the author had tried any such cell in which light, simply and solely, generated an E.M.F. He could not agree that chemical action must necessarily follow the action of light in a cell. For take the case of the oldest photo-electric cell,—the thermopile,—what chemical action can we show here for all the energy of the incident heat? Chemical action due to light may or may not occur, according to the nature of the cell.

Mr. APPLEYARD asked whether the author had submitted these selenium resistances to the action of electric oscillations. Prof. Minchin's "impulsion" cells were greatly influenced by electric oscillations. The great variation in the resistance with time of the author's cells pointed rather to an effect of contact between the selenium and the electrodes than to an elementary change in the structure or composition. He (Mr. Appleyard) had recently tried to crystallise a supersaturated solution of sodium sulphate by electric oscillations, as well as by direct sparks, and by currents of several amperes; but no crystals could be induced to form. Change of contact rather than change of structure appeared to him to be the most promising direction in which to look for an adequate theory of selenium resistances.

Prof. RAMSAY said the quantity of Se liberated in the electrolytic experiment was much too great to be accounted for by oxygen dissolved in the water. The study of Se was very interesting, for this substance was on the border-land between those bodies in which the electric conduction was metallic and those in which it was known to be electrolytic.

The author, in his reply, said he agreed that the name "selenium cell" was not an appropriate one. He had not tried the effect of electric oscillations.

The Society then adjourned till the autumn.

NOTICES OF BOOKS.

The Century Science Series. John Dalton and the Rise of Modern Chemistry. By Sir HENRY E. ROSCOE, D.C.L., LL.D., F.R.S. London, Paris, and Melbourne: Cassell and Co., Ltd. 1895.

THE position of Dalton in the history of science is now so fully established and so universally conceded that it requires no discussion, especially as his career has been already described by W. C. Henry, R. A. Smith, H. Lonsdale, J. Harland, C. Wheeler, and F. Espinasse.

The author pronounces Dalton to be the "founder of modern chemistry," and Joule to be the "founder of modern physics."

But it is strange that these two illustrious savants are pronounced to be "Manchester's two greatest sons," to be the "great twin brethren of Manchester," while all the time Dalton was born in the remote Cumberland village of Eaglesfield, and did not become a dweller in Manchester until the age of twenty-seven. Hence, whatever may be said concerning Joule, Dalton was certainly not one who "arose in the midst of a population given up to industrial pursuits, . . . and where most men's thoughts are engrossed in what shallow minds often look upon as common trade avocations." We must here note with regret the political and semi-political remarks introduced, the more gratuitously since Dalton was not a

politician, but seems to have wisely felt that the position of the philosopher, as of the poet, "should be higher than on the battlements of party."

It is interesting to find that Dalton, in his pre-Manchester days—if we may coin such an expression, in addition to meteorology, gave some attention to botany and entomology, and his collections remained for some time in the Keswick Museum.

After arriving in Manchester, Dalton published an English grammar, which soon disappeared from circulation. But a Sheffield man re-published it some years afterwards as his own.

Dalton seems to have predicted, before the earliest experiments of Faraday in that direction, that the gases would ultimately be condensed by low temperature and strong pressure.

A chapter is devoted to his remarkable optical defect of colour-blindness, to which he drew attention in a memoir. By a singular piece of bad taste, not a few Continental authorities thought fit to call this defect "Daltonism."

The investigations which led to the "atomic theory" were entered upon early in the present century. In a lecture delivered in January, 1810, he expressed the opinion that the elements are periodical and absolute:—"I should apprehend," he writes, "that there are a considerable number of what may properly be called *elementary* principles which can never be metamorphosed one into another by any power we can control." Still he holds that "we ought to avail ourselves of every means to reduce the number of bodies or principles of this appearance as much as possible."

An account is given of the reception of the atomic theory by other chemists and of the attitude of Dalton towards the theories of others, such as Gay-Lussac and Avogadro. This attitude was generally unfavourable. He would not admit that there are the same number of particles of a gas in a given volume and under a given pressure.

The remaining chapters contain much interesting matter. We learn that, being once unwell, "his doctor ordered a dose of James' powder. Next day the patient was better, and the doctor attributed the result to his prescription. 'I do not well see how that can be,' said Dalton, 'for I kept the powder until I could have an opportunity of analysing it.'" Though not a total abstainer, he seems to have come practically to the same opinion as von Helmholtz, who found that the slightest quantity of alcohol drove away any chance of his "arriving at any new and good scientific idea."

It is recorded that he was the first to introduce the process of volumetric analysis. He became a Fellow of the Royal Society in 1822, and received the first Royal Medal in 1826. It almost sets one's teeth on edge to learn that when Dalton was presented at Court, King William the Fourth could think of nothing more appropriate to say than:—"Well, Dr. Dalton, how are you getting on at Manchester—all quiet, I suppose?"

Notwithstanding the existence of other memoirs of Dalton, this little work deserves warm recommendation.

A Treatise on Practical Chemistry and Qualitative Analysis. Adapted for Use in the Laboratories of Colleges and Schools. By FRANK CLOWES, D.Sc., Professor of Chemistry at the University College, Nottingham; Member of the Councils of the Institute of Chemistry and of the Society of Chemical Industry; Fellow of the Chemical Societies of London and Berlin. Sixth Edition. Crown 8vo., pp. 469. London: J. and A. Churchill. 1895.

THIS work holds a convenient intermediate position between the bald epitomes which are now so common and the elaborate works of Fresenius, Rose, &c. Having already passed through the ordeal of six editions, it may be considered as in harmony with general requirements.

It has the advantages that the rarer elements are not ignored, special tables being furnished for their recognition. Instructions are given for the detection of organic acids, alkaloids, and other organic substances. The use of the blowpipe, the microscope, and the spectroscope is kept in view. The student is recommended to buy pure reagents, rather than to attempt their preparation, which will in general involve a great outlay of time.

In nomenclature little need be said. Glucinum has, we believe, the claim of priority, as against beryllium, used by the author. "Mercuria acid" must, however, we submit, be merely a compositor's error.

The illustrations of apparatus and of laboratory arrangements are excellent, as are also the accompanying remarks on manipulation.

Theoretical explanations are very properly relegated to works on descriptive chemistry. The work, in short, merits almost unqualified recommendation, though we may regret the homage paid to the Chinese system in the preface.

The Law of Copyright in Designs; together with the Practice relating to the Proceedings in the Courts and in the Patent Office, and a full Appendix of Statutes, Rules, and Forms, the International Convention, &c. By LEWIS EDMUNDS, D.Sc., LL.B., F.C.S., and F.G.S., Barrister-at-Law; assisted by T. M. STEVENS, B.C.L., and MARCUS W. SLADE, B.A., Barristers-at-Law. London: Sweet and Maxwell. Manchester: Meredith, Ray, and Littler. Dublin: Hodges, Figgis, and Co.; and Ponsonby. Melbourne and Sydney: C. F. Maxwell. 1895. 8vo., pp. 291.

THE registration of designs is a method for securing a proprietary right, complementary to patents for inventions. The number of designs registered annually is here stated as about 20,000. It appears that, after several tentative enactments, copyright for three years was granted to any new and original design, whether such design be applicable to the ornamenting of any article or for the shape or configuration thereof, and however it is produced or applied. The classes of manufacture are articles of metal, wood, glass, earthenware, paperhangings, carpets, shawls, tissues, &c. In 1883 the previous Acts were repealed, and the provisions of the Patents, Designs, and Trade-marks Acts substituted. The decisions under these Acts have been few, and it is admitted that many ambiguities still remain.

The question is raised, What is a design? Then arises the question of novelty.

Next follows publication, which may be effected in a variety of ways. We come then to the question of proprietorship. There are, it seems, five classes of persons who may be considered proprietors: the author of the design; any person who employed the author to execute the work for good and valuable consideration; any person acquiring the design for such consideration; a person acquiring the right to apply the design to articles; and, lastly, persons on whom the design on these rights may devolve.

There is an elaborate section on infringement and the remedies.

In Part II. is given the text of the Patents, Designs, and Trade-mark Acts from 1883 to 1888, so far as they relate to designs, followed by the designs rules of 1890 and 1893, and the details of the International Convention for the Protection of Industrial Property.

The Appendices include the Statutes concerned; the forms; instructions to persons wishing to register designs; and Orders in Council applying the provisions of the Patents, &c., Acts, to British Possessions and Foreign States.

Lastly, follows a bibliography of the literature of copyright in designs.

The book, though of less interest to the majority of our readers than the authors' companion volume on Patents

for Inventions, will prove highly valuable to counsel and solicitors, and more especially to patent agents.

The Prospector's Handbook. A Guide for the Prospector and Traveller in Search of Metal-bearing or other Valuable Minerals. By J. W. ANDERSON, M.A., F.R.G.S., F.L.Inst., Author of "Fiji and New Caledonia." Sixth Edition, thoroughly Revised and much Enlarged. Fcp. 8vo., pp. 176. London: Crosby Lockwood and Son. 1895.

THIS handy little book ought to be the pocket-companion of every frontier-man and explorer of the Far South. It will, we believe, guard the prospector against two opposite evils, viz., collecting and carrying away matter of no value and overlooking precious deposits. Both these mistakes have been very often made; yellow micas and certain pyrites have been taken for gold, and, on the other hand, platinum, nickel, and cobalt have been tossed aside as worthless. The author's advice is the more valuable because he is not a mere compiler, reproducing the work of others in different language, but a field-geologist, who has gained experience in New Zealand, New Caledonia, Mexico, and the Western States of America.

A valuable feature of this little book is, that it makes a minimum demand upon the scientific or technical knowledge of the prospector, as well as upon his funds and upon his means of conveying apparatus. Processes which are excellent in a fixed laboratory are worthless if they require the use of heavy and delicate instruments. The use of the blowpipe is very justly recommended. But we would suggest that a pocket spectroscope and a good lens will occasionally prove useful without making an objectionable addition to the traveller's impedimenta.

We are glad to notice that, among the substances to be sought for, coal and petroleum are not disregarded.

Vanadium has been overlooked; but it is perhaps more likely to occur among furnace-products, &c., than in native rocks. Nor do we find any mention of potash. Our present commercial supply of this requisite, so necessary alike to the chemical manufacturer and the farmer, is confined to Germany. Hence we suggest that it should be earnestly sought for in the Dominion, Australia, and Africa.

An excellent feature of the work consists in the practical hints which are scattered through it, and which will often direct the prospector to search in right places.

Another useful feature is the glossary of terms used in different countries by miners, metallurgists, &c.

But there is the less reason for us to enlarge on the striking merits of Mr. Anderson's work as it has already reached its sixth edition.

Year-Book of Electro-chemistry. ("Jahrbuch der Elektrochemie.") Reports on the Advances of the Year 1894. The scientific part elaborated by W. NERNST, Professor in Ordinary at the University of Göttingen, Director of the Institute for Physical Chemistry and Electro-chemistry. The technical part elaborated by Dr. W. BORCHERS, Teacher at the Duisburg Royal School for Machinery and Foundries. Vol. I. 8vo., pp. 274. Halle: W. Knapp. 1895.

THIS work affords a useful summary of the progress effected in electro-chemistry during the year 1894. Prof. W. Nernst first expounds the general scientific points of view which are now accepted.

We find a notice of the researches of Kohlrausch and Heydweiller on the conductivity of pure water. It had been previously shown by the former that water becomes less conductive the more carefully it is purified. It is now proved that finally a limit is reached, or, in other words, that water has a specific conductivity.

In the second part of the work Dr. Borchers discusses the applications of electro-chemistry. He begins with

an account of the production of electric energy from chemical energy.

Prof. Ostwald, in a brilliant discourse delivered before the Congress of German Electro-technicians (*Zeit. Elektro-techn. und Electrochemie*, 1894, Parts 3 and 4), expressed himself to this effect:—"The way in which may be solved the greatest of all technical questions, the production of cheap energy, must be discovered by electro-chemistry. If we have a galvanic element which furnishes directly electric energy from carbon and the oxygen of the atmosphere, in a quantity fairly proportionate to the theoretical value, we have a technical revolution in comparison with which the invention of the steam-engine must vanish. Only conceive what will be the aspect of our industrial places in view of the incomparably convenient and flexible distribution of which electricity is susceptible. No smoke, no soot, no boilers, no engines, even no fire, since fire will be needed only for the few processes which cannot be conducted electrically." Every chemist will hope that this ultimate prospect is not too fascinating to be realised.

In discussing electrolytic depositions and separations the author quotes (*Zeit. Elektro-techn. und Electrochemie*, 1894, 6 and 9, and *Chem. Zeit.*, 1894, Nos. 59 and 71) the complete worthlessness of Rüdorff's directions concerning the current to be applied. The author is of opinion that the prolonged action of Meidinger elements, as recommended by Rüdorff, is not sufficiently constant. He recommends the use of illuminating currents as used for electro-chemical analysis in the laboratory of the High School at Stockholm. Few laboratories possess the motive power for dynamos, and still fewer are not deterred by the expense and the inconvenience of accumulators.

Concerning Hermite's "so-called disinfecting and sanitary processes,"—treatment of sewage,—the most trustworthy accounts are not favourable.

In the application of electrolysis to dyeing there is no novelty of value to be mentioned, the patented processes of Skuzcek and Zelen having been long previously anticipated by Goppelsröder.

No one can doubt that we are, to say the least, on the threshold of surprising modifications and improvements which will be due to the applications of electricity in the chemical arts.

City and Guilds of London Institute for the Advancement of Technical Education. Report to the Governors, March, 1895. Gresham College, Basinghall St., E.C. 1895.

MOST of our readers will already be acquainted with the general constitution of the City and Guilds of London Institute, and with the movement of which it is at once the seat and the embodiment. We have here a list of the Governors, including the *ex-officio* members of this body, the Presidents of the Royal and the Chemical Societies, of the Council of the Society of Arts, and of the Institution of Civil Engineers. The President of the Institute of Chemistry is not here included. Then follow the representatives of the Corporation and of those Guilds who are taking part in the promotion of technical education, *i.e.*, the Mercers', Grocers', Fishmongers', Goldsmiths', Merchant Taylors', Salters', Ironmongers', Vintners', Clothworkers', Dyers', Leather-sellers', Pewterers', Cutlers', Armourers' and Braziers', Saddlers', Carpenters', Cordwainers', Plumbers', Coopers', and Plasterers' Companies. In these lists figure among others the honoured names of Mr. G. Matthey, F.R.S., Sir F. Abel, F.R.S., Sir J. D. Hooker, F.R.S., &c. Next follows the Council, comprising most of the above, and the Executive Committee.

The Staff of the Institute's Colleges includes, in pure chemistry, Prof. H. E. Armstrong, F.R.S.; and H. A. Miers, M.A., as instructor in crystallography, besides assistants and a demonstrator. The Staff for applied chemistry comprises Prof. Raphael Meldola, F.R.S., &c., with two demonstrators and a lecture assistant.

We notice certain very encouraging features. Unlike the majority of British schools, the Institution gives as its "results," not the names of pupils who have "passed" some examination, but of former students who have proved, and are still proving in after life, the soundness of the training they have received. Among these sixteen former students in the chemical department receive prominent mention. Chemistry is, however, by no means a favourite subject. Thus of the 186 ordinary students for the Session 1893-94 only 20 are studying chemistry, as compared with 71 engaged in engineering and 95 in physics.

The total number of students attending the day-classes shows a falling-off as compared with the previous session, when the number was 213. Of the day-students, 197 in number, 70 had been previously educated at grammar and other endowed schools; at middle class schools, 69; at private schools, 48; and at public elementary schools, *i.e.*, board and church schools, only 10. Of the 992 evening students attending the College, 39 were engaged by day in the chemical industries. This number is small, but we must remember that these industries occupy in London only a relatively small number of persons.

A glance at the sums presented and subscribed in support of the Institution by the City Companies might be a wholesome lesson for some persons who are in the habit of telling their ignorant hearers that the Guilds expend their resources in riotous living, and that their funds ought to be confiscated for the promotion of fads. It appears that the total amount contributed by these much-slandered bodies, and some of their leading members, has been £453,435 19s. 6d. Of this total £78,964 have been contributed by the Goldsmiths, £68,250 by the Clothworkers, and £66,550 by the Fishmongers. These figures do not include the sums contributed by, *e.g.*, the Clothworkers' Company, towards the technical departments of the Yorkshire College. We find, to our great satisfaction, that the Salters' Company have placed at the disposal of the Institute a sum of £150 yearly, to be applied to founding one or more Fellowships, to be entitled the Salters' Company's Research Fellowships, for the encouragement of higher research in manufacturing chemistry. The first award under this scheme was made in January last, to Martin O. Forster, Ph.D., F.C.S. Dr. Forster had been a chemical student at the Finsbury Technical College during the Sessions 1888-91, and has subsequently graduated at the University of Würzburg.

Mr. F. H. Carr is now a Salters' Company's Research Fellow, in the Research Laboratory of the Pharmaceutical Society.

But though satisfactory progress is being made, we must not, as a nation, forget the immense ground we have to recover, and the energy and means which we have wasted over the cram and the examination systems.

How much good might be effected if the friends of scientific instruction had at their disposal the large sums which are still being squandered by the various "anti" movements, and in the promotion of valueless fads. The City and Guilds of London Institute is, we are happy to say, not a cramming school.

CORRESPONDENCE.

MYSTERIOUS DISAPPEARANCE OF PECTOSE.

To the Editor of the Chemical News.

SIR,—Would some of your readers kindly inform me why have pectose, pectonic acid, and all the other pectose bodies, disappeared from all modern works on organic chemistry, except the last edition of "Watts' Dictionary of Chemistry"? Had they ever any existence except in text-books, or were they mere mixtures of gums and sugars?—I am, &c.,

CARBO-HYDRATE.

USE OF MINERAL OIL FOR EXCLUDING
AIR IN PAVY TITRATIONS.*To the Editor of the Chemical News.*

SIR,—In my letter on the above subject (CHEMICAL NEWS, lxxii., p. 11) there is an erratum of a rather important nature. Instead of saying that "at the time when the abstract appeared I was not aware of the existence of Professor Brauner," what I actually wrote was that "I was not aware of the residence of Professor Brauner."—I am, &c.,

ALFRED H. ALLEN.

Sheffield, July 6, 1895.

BRAZILIAN MONAZITE.

To the Editor of the Chemical News.

SIR,—My attention has just been called to an article in the CHEMICAL NEWS (vol. lxxi., p. 181) entitled "North Carolina Monazite," by H. B. C. Nitze. In it he remarks that monazite is found in paying quantities in Brazil.

May I venture to ask that gentleman, through your columns, if he knows in which State of Brazil that mineral is found? If so, would he have any objection to furnishing me with the information?—I am, &c.,

J. MACDONALD KYLE.

The Laboratory,
Usina Wigg, Miquel Burnier,
Minas Geraes, Brazil, June 12, 1895.

CHEMICAL NOTICES FROM FOREIGN
SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Zeitschrift für Analytische Chemie.
Vol. xxxiii., Part 5.

Crystalline Hard Combinations in Cementation Steel, and in Alloys of Iron with Chromium, Tungsten, and Manganese.—H. Behrens and A. R. von Linge.—This article commences with an account of the microscopic examination of the metals in question, viz., of crude cement steel, obtained from puddled Dannemara iron; of ferro-tungsten and tungsten-steel; of ferro-chrome, chrome-steel. Then follows an account of the analysis of the metals, qualitative and quantitative.

Sensitiveness of some Zone Reactions, and their Application in the Recognition of Acids.—Hein. Trey.—If the more frequently occurring inorganic acids, including oxalic acid, are grouped in such whose silver compounds are precipitated from acid solutions, such as hydrochloric, hydrobromic, and hydriodic acid, iodic acid, hydrocyanic, hydroferrocyanic, ferricyanic, sulphocyanic, and hydrosulphuric acid; and, further, in such whose silver salts are only deposited in neutral solutions, such as phosphoric, arsenic, arsenious, chromic, oxalic, boric, sulphurous, thiosulphuric, and silicic acids. If we, secondly, divide the acids precipitable by barium, or calcium chloride again into such whose barium salts are precipitated from hydrochloric solutions, i.e., sulphuric and selenic, and hydrofluosilicic acid; and into such whose barium or calcium salts are sparingly soluble in acetic acid, i.e., oxalic, chromic, and hydrofluoric, their detection may be more easily and simply effected as follows:—If the alkaline solution obtained by boiling in sodium carbonate, the original substance—supposed to be soluble in water or other acids—and if silver nitrate is then added in excess, the first mentioned silver compounds of the acids insoluble in nitric acids are precipitated. If we then filter, and add to the filtrate ammonia in such a manner as to superstratify the solution, so that the am-

monia, which is specifically lighter, remains floating in the upper part of the test-tube, there appears at the surface of contact of the two liquids a neutral zone, in which place, in presence of the above-mentioned silver salts of the acids precipitable only in a neutral solution, either as a precipitate or as a slight turbidity. If, in the same manner, we add to another part of the alkaline solution hydrochloric acid until the reaction is acid, and then barium chloride, the precipitate formed shows the presence of the above-named acids, which precipitate as barium salts from a hydrochloric solution. If we now add to the filtrate calcium chloride, in order to obtain any oxalic acid or hydrofluoric acid as calcium salts, which are much less soluble than their barium compounds, and if we convert the solution into an acetic liquid by the addition of sodium acetate, we obtain the precipitates of the barium or calcium compounds of the above-named acids, i.e., barium chromate, calcium oxalate, and barium or calcium fluoride. If we set aside those of the acids previously enumerated which have already been detected in searching for the bases, or in dissolving or acidifying the original substance, such as sulphurous acid, thiosulphuric acid, iodic acid, and hydrogen sulphide, the presence of which, moreover, is not possible in an acid solution; if we boil, after the addition of nitric or hydrochloric acid, the proposed method for detecting the groups of acid in question may be given thus:—

Acids Precipitable by Silver Nitrate.

From nitric solution.	From neutral solution.
Hydrochloric acid.	Phosphoric acid.
Hydrobromic acid.	Arsenic acid.
Hydriodic acid.	Arsenious acid.
Hydrocyanic acid.	Chromic acid.
Hydroferrocyanic acid.	Oxalic acid.
Hydroferricyanic acid.	Silicic acid.
Hydrosulphocyanic acid.	Boric acid.

Acids Precipitated by Barium Chloride.

From a hydrochloric solution.
Sulphuric acid.
Selenic acid.
Hydrosilicofluoric acid.

Acids Precipitated by Barium and Calcium Chloride.

From an acetic solution.
Chromic acid.
Oxalic acid.
Hydrofluoric acid.

If the liquid is boiled after the addition of nitric acid (boiling is to be recommended after the addition of silver nitrate, in order to obtain a clear filtrate more easily and quickly), the solution must be allowed to cool before adding the ammonia, as on superstratifying the hot filtrate with ammonia at the ordinary temperature the lower current will stream into the upper, and thus render the superstratify an illusion. This method is satisfactory and easy, only the students are supplied with binormal solutions; that is, such as contain per litre double the equivalent—expressed in grms.—of acid alkali, or salt.

Detection of Iodine in Urine.—Dr. A. Jolles.—The author has obtained satisfactory results by the two following methods indicated by Sandland (*Archiv der Pharmacie*):—1. Precipitating with silver nitrate the specimens acidulated with silver nitrate, reducing the precipitate with zinc and hydrochloric acid, distilling the solution obtained with ferric chloride, receiving the distillate in solution of potassium iodide, and titrating with centi-sodium thiosulphate solution. 2. Evaporating the urine in a platinum capsule on the water-bath after the addition of sodium carbonate, charring and incinerating the residue, slightly acidulating the aqueous solution with dilute hydrochloric acid, and distilling with ferric chloride.

On Oils.—G. de Negri and G. Fabris (translated from the original Italian by Dr. Holde).

THE CHEMICAL NEWS.

VOL. LXXII., No. 1860.

HELIUM.

By WILLIAM HUGGINS, F.R.S.

With the advantage of a bluer sky than I had during my former observations, I saw the fainter component of D_3 to-day. In the chromosphere, close to the limb, both lines are usually expanded, so that the interval between them is very small, and on that account less easy to see. At a little distance from the limb, and especially in suitable prominences, the lines become thin, when the fainter component is easily overpowered if there is much scattered light from haze or thin cloud. D_3 was seen double both near the limb and in a prominence.

I hear that Professor Hale has already seen the solar line double in the United States.

90, Upper Tulse Hill, S.W.,
July 10, 1895.

THE ANALYTICAL CHARACTERS OF A MIXTURE OF SALTS OF BARIUM, STRONTIUM, AND CALCIUM.

By H. BAUBIGNY.

In the determination of the elements present in a saline solution, the detection of the three alkaline earthy metals, barium, strontium, and calcium, is often regarded as delicate. The fact is due merely to the defective character of the methods employed, or to a want of precision in the procedures indicated.

Let us suppose that all the metals precipitable by ammonium sulphide are eliminated, operating in presence of sal-ammoniac to favour their separation. In the liquid we transform, as usual, the three alkaline earthy metals into insoluble carbonates by means of ammonium carbonate. We filter and wash with a dilute hot solution of ammonium chloride. The filtrate will then contain merely the alkaline metals, and magnesium if present.

The mixture of the three insoluble carbonates is redissolved with hydrochloric acid, which is added slowly and drop by drop, so as to have a liquid which is neutral, or approximately so. A small excess of acid may be corrected, if needful, by the addition of a proportionate quantity of an alkaline acetate. Under these conditions potassium dichromate precipitates merely the barium, and indeed *all the barium*, the chromate of which is insoluble in free chromic acid or in very dilute acetic acid. We cannot, in a neutral medium, operate with the yellow alkaline chromate, which precipitates equally the salts of strontium, and even those of calcium if concentrated.

We then recognise the strontium by adding to the filtrate a solution of potassium sulphate containing 2.5 grms. of the salt per litre, and in the sole case of the presence of strontium there is a precipitate after agitating for a few seconds.

The concentration of the solution of alkaline sulphate is such, in fact, that the calcium sulphate which might be formed is in presence of a quantity of water more than sufficient to keep it in solution. If there is only calcium present there is the less trouble; moreover, the use of the alkaline sulphate, substituted for that of calcium sulphate, has the advantage of permitting the search for calcium in the same liquid. The strontium sulphate thus obtained has always a yellowish cast, due to a little strontium chromate carried down, in spite of the solubility of this latter salt in the conditions of the process.

To detect the calcium it is necessary to eliminate the chromic acid, as it would vitiate all the remaining operations. To this end, in the filtrate from the strontium sulphate we precipitate in heat the calcium and the residue of the strontium by means of potassium carbonate; we re-dissolve the carbonate, little by little, with hydrochloric acid, correcting the excess of acid, if requisite, with ammonium acetate. To the solution we add a large excess of sal-ammoniac, either in crystals or in a concentrated solution, and a few drops of potassium ferrocyanide.

There is formed at first a turbidity, then a precipitate, which increases rapidly, and which, according to Rose, is a double compound of potassium and calcium ferricyanide, sparingly soluble in water, and insoluble in ammonium chloride. The sensitiveness is such that a solution of calcium sulphate, with the addition of three to four times its volume of water saturated with sal-ammoniac, is rendered strongly turbid, and precipitated after being stirred up for a minute with a little potassium ferrocyanide.

The salts of strontium produce nothing similar even in a highly concentrated solution; the liquid remains perfectly clear. Still we cannot think of employing this method for the separation of the two metals, since strontium is always carried down, and even if the calcium is in decided excess the totality of the strontium is found in the precipitate.

Barium gives with ferrocyanide the same reaction as calcium, although the sensitiveness is much less even with the use of sal-ammoniac. It is therefore preferable, for greater accuracy, to separate firstly the barium.

These facts having been explained, it is easy to understand the necessity of removing chromic acid after the separation of the barium, in order to detect calcium in presence of strontium. Free chromic acid oxidises ferrocyanide to the state of ferricyanide, and finally there remains merely neutral alkaline chromate, which occasions the formation of insoluble strontium chromate, whilst at the same time there is produced double potassium and calcium ferrocyanide by the slightest excess of ferrocyanide, the ferricyanide having no action, and thus every conclusion is wanting in the desirable accuracy.

In the case where the existence of calcium is the only question of interest, we heat at first with a concentrated solution of alkaline sulphate; the filtrate then contains sufficient calcium to permit of its detection by ferrocyanide.

This remark leads to a variation in the method indicated for the detection of the three alkaline earthy metals. After having recognised barium by potassium bichromate, and then strontium in the filtrate by the standard solution of potassium sulphate (2.5 grms. per litre), we precipitate the rest of the strontium with a concentrated solution of the same sulphate, filter, saturate the liquid with ammonium chloride, and add ferrocyanide in excess to destroy the free chromic acid. As strontium then no longer exists it cannot form a chromate, and consequently if there is a precipitate it is exclusively due to calcium by the action of the ferrocyanide.

The solubility of the carbonates of these metals in ammonium chloride has been an objection to the precipitation of the earthy alkaline metals by ammonium carbonate in presence of a large excess of sal-ammoniac. If this fact is important in a quantitative respect, there is no reason to exaggerate this importance in ordinary qualitative determinations. In fact, a solution of calcium chloride at 1 part in 1000, and containing 50 per cent of the sal-ammoniac which it can dissolve—that is to say, half saturated—certainly gives only a scarcely perceptible turbidity with ammonium carbonate; but if we add ammonia to destroy the bicarbonate which always exists, and apply heat, there is produced a very appreciable action. It is the same with barium and strontium.

Even when reduced to these slight proportions the qualitative analysis is not always defective. Still expe-

rience has taught me that in these limits it is advantageous to modify the process a little. Let us suppose that the liquor charged with sal-ammoniac contains quantities of barium, strontium, and calcium, only in the proportions of thousandths of the weight of that of the solvent. Under such conditions neutral chromate precipitates neither lime nor strontia. If this reagent gives a precipitate it is because barium is present. After stirring and waiting for a few moments we filter. All the barium having been separated, we treat with a drop of sulphuric acid; if strontium is present, a precipitate of sulphate is quickly formed.

Lastly, in another portion of the liquid, which must be saturated with ammonium chloride, we try the reaction with potassium ferrocyanide; a solution of barium (1 part in 1000) giving nothing, whilst with calcium, even at a strength considerably inferior, we have still a very decided opalescence.

Another difficulty in presence of a great excess of sal-ammoniac, if we have a solution very rich in magnesium, is, that on the addition of ammonium carbonate and ammonia, there may occur a separation of the double ammonium and magnesium carbonate. But it is very easy to obviate this inconvenience by diluting the liquid or re-dissolving the precipitate and then adding a hot and dilute solution of ammonium chloride, which re-dissolves the double carbonate. Hence I recommend the precipitate to be washed with hot water slightly charged with sal-ammoniac. Let us add, *e.g.*, to 5 c.c. of a solution of ammonium chloride saturated in the cold, 3 to 5 c.c. of a solution of magnesium chloride (at 1 part in 10); then a little ammonium carbonate and ammonia; the liquid becomes turbid, and in heat the precipitate increases, whilst it disappears if we double the volume by the addition of water. If we have employed only 1 c.c. of magnesium chloride (the proportions of the other substances remaining the same), the precipitate formed in the cold, on the contrary, disappears in part without the addition of water, and the liquid then remains perfectly clear. The proportion of magnesium has, therefore, its importance.

In conclusion, I must point out that no method for the separation of strontium and calcium can be founded upon the simultaneous use of potassium oxalate and carbonate, so that the strontium would be converted into carbonate and the calcium into oxalate, and, after washing, separating by the aid of acetic acid, in which calcium oxalate is distinctly insoluble.

The action in the cold varies, in fact, with the proportions of the two alkaline salts employed. For an excess of oxalate (3 parts to 1 of carbonate), we have only oxalates; for an excess of carbonate (3 parts to 1 of oxalate), almost all the calcium is in the state of carbonate, and the action does not seem more distinct with a mixture of equal parts.

At a boiling heat, in all cases, even if there is a decided excess of oxalate, the action of the alkaline carbonate always predominates both for calcium and strontium.—*Bulletin de la Soc. Chim. de Paris.*

ON AN EXPLOSION: AS A WARNING.

By EUG. BAMBERGER.

My assistants have since last summer prepared the crystalline *p*-nitrodiazobenzene nitrate dozens of times, pressing the substance energetically on the clay plate and rubbing it with the horn spatula without the slightest explosive phenomenon having ever been perceptible. The salt is extremely less explosive than the ordinary diazobenzene nitrate. Whilst a very small quantity of the latter detonates loudly if heated, an equally small quantity of the nitro-derivative deflagrates only with a relatively feeble report. We have frequently rubbed up the

salt upon porous earthen plates in quantities of 30 to 40 grms. without any precaution.

Unfortunately a fearful explosion has lately occurred which seems scarcely to be reconciled with previous experience, and the causes of which are not explained with certainty. F. Goose had prepared about 20 grms. of the salt by the direction of my private assistant, Dr. Meimberg, and was gently turning the crystals over on a smooth earthen plate with a glazed porcelain spatula, which had no sharp corners or edges, when suddenly there ensued an explosion with a fearful noise and the most destructive effect. F. Goose lost eight fingers—some entirely and others partially. The sight of his left eye has suffered severely. He cautiously, as he had to do with a diazo-salt, avoided all pressure or rubbing. Since this misfortune we have repeatedly rubbed the nitrate with the porcelain spatula upon clay without any explosion.

F. Goose remembers distinctly that his preparation contained some black sandy grains, which he had chiefly, though not entirely, picked out, and which—as he believes—were derived from the snow used for refrigeration.

Dr. Meimberg has, in fact, been able to produce an explosion by a prolonged grinding up of the salt with remnants of gritty snow. It is merely remarkable that F. Goose should encounter this misfortune on gently and loosely turning it over.

By this opportunity I should wish to give a warning against paranitroisodiazobenzene hydrate. This substance has recently exploded, although nothing of the sort was apprehended, as it was being laid in a pulverised and dried state upon a card paper for the purpose of weighing. There ensued merely a deflagration with a dull report; still it will always be advisable, when working with this substance, to protect the eyes.—*Berichte*, xxviii., No. 6.

A METHOD FOR THE VOLUMETRIC ESTIMATION OF THE PHOSPHORIC ACID, SOLUBLE IN WATER, PRESENT IN SUPERPHOSPHATES.*

By W. KELMAN and K. MEISSELS.

ON titrating a solution of phosphoric acid with some normal soda and methyl-orange as an indicator, the final reaction occurs as soon as the salt NaH_2PO_4 is formed,—that is, when one-third of the acid is saturated. If we use phenolphthalein as the indicator, the red colour appears on the formation of the salt Na_2HPO_4 . In the acidimetric titration of a solution of acid calcium phosphate, which has a neutral reaction with methyl-orange, there occurs the following transposition:—

$3\text{CaH}_4(\text{PO}_4)_2 + 8\text{NaOH} = \text{Ca}_3(\text{PO}_4)_2 + 4\text{Na}_2\text{HPO}_4 + 8\text{H}_2\text{O}$, when the calcium phosphate is eliminated; 8 mols. NaOH here, therefore, behave as equivalent to 3 mols. P_2O_5 . On titrating superphosphates with the assumption of the above transposition, we sometimes, however, obtain differences which show that the various salts present in the superphosphates behave differently to the lime salts, and that a calculation according to the above equation is not valid.

This difficulty can be overcome on the basis of the following consideration:—If we titrate a solution containing acid calcium phosphate, with phenolphthalein as the indicator, and assume, according to the rule of saturation, that 1 mol. NaOH saturates $\frac{1}{2}$ mol. P_2O_5 , we obtain on titration too high results; but if, after obtaining the final reaction with phenolphthalein we filter the liquid off from the precipitate, add methyl-orange, and titrate back with acid, the results of this

* Communication of the Technol. Museum of Vienna, 1894 (*Zeitschrift für Anal. Chemie*, xxxiii., p. 764).

titration will be as much too low as those of the former operation were too high. The arithmetical mean of both titrations will give the correct result.

On the basis of these considerations the authors proceed as follows:—20 grms. superphosphate are dissolved, *secundum artem*, to 1 litre. (a.) 100 c.c. of the filtrate are mixed with methyl-orange, and exactly neutralised with some normal lye. Phenolphthalein is then added to the same solution, and semi-normal lye is added until the change of colour and the quantity required are accurately noted. This titration requires great attention, since the precipitate during its formation interferes with the recognition of the final reaction. (b.) Further, 100 c.c. of the solution of superphosphate are mixed in a 250 c.c. flask with a sufficient excess of semi-normal lye, filled up to the mark, shaken up, and filtered. 100 c.c. of this filtrate are mixed with phenolphthalein, neutralised with semi-normal acid, methyl-orange is added, and the liquid is exactly titrated with semi-normal acid. The number of c.c. used must be multiplied by 2.5, in order to obtain the quantity representing 100 c.c. solution of superphosphate.

The arithmetical mean of (a) and (b) multiplied by 0.0355 gives the grms. of P_2O_5 in 100 c.c. of solution of superphosphate = 2 grms. of the substance.

SIMPLIFIED METHOD FOR DETERMINING PHOSPHORIC ACID BY MEANS OF MOLYBDENUM SOLUTIONS.

By Dr. J. HANAMANN.

As the molybdic method permits the most accurate determination of phosphoric acid in phosphoric liquids, and serves as a check-method for all other determinations of phosphoric acid, but has merely the defect of a double precipitation and of the tedious conversion of the molybdenum precipitate into magnesium pyrophosphate, the efforts of analysts have for some time been directed to its simplification and its conversion into a volumetric form. But the gravimetric determination of phosphoric acid is at present so generally demanded that we have been compelled in case of superphosphates to adopt, in place of the molybdic method, the citrate method, which requires one precipitation only, though in certain phosphoric liquids rich in lime it gives values in excess.

The yellow phospho-molybdic compound has hitherto not been esteemed of constant composition, because, on heating the phosphoric precipitates, molybdic acid in excess is added to the subsiding precipitate, and is thrown down conjointly. We have either to precipitate a part of the molybdic acid by previous repeated boilings from a molybdic solution obtained on Sonnenschein's method, and then effect the precipitation of the phosphatic solution in heat, with the molybdic solution overcharged with nitric acid,—or we must make use of such a molybdic solution as deposits, in the cold and after prolonged agitation of the mixed liquids, all the phosphoric acid of the solution as a molybdic precipitate of a constant composition.

In fact, it is practicable to throw down in the cold, and after vigorous stirring for thirty minutes at common temperatures, from a solution containing to 100 grms. molybdic acid, 1 litre of 10 per cent ammonia, and 1½ litres of nitric acid at 1.246 sp. gr., as also from the Maercker solution after the addition of ammonia. This is effected in such a manner that the precipitate, washed with ammonium nitrate and nitric acid and dried, and gently ignited, has a pure black-blue colour, a constant composition, and contains—in 100 parts by weight—4.018 phosphoric acid. The differences in weight of the precipitate at the various changes of colour from yellow to black are as follows:—

	Grms.
Orange	35.2325
Greenish	35.2140
Black, blue, greenish in the middle	35.2050
Uniform black-blue.. .. .	35.2010
Tare	33.9520
	1.2490

Twenty-five c.c. of the solution of sodium phosphate used, treated with the above-named molybdic solution in the manner described, gave a black-blue precipitate weighing 1.245 grms., which, multiplied by 0.04018, $0.050 = 1.84 \times 2$, therefore in 50 c.c. = 0.10036 phosphoric acid; 50 of this solution contained 0.1 gm. phosphoric acid. By this method we may examine high-class superphosphates, and such as contain iron, as well as arable soils.

The recent smooth dense filters of the firms Dreverhoff, and Schleicher and Schüll, permit of a very complete removal of the precipitate from the filter, and the separate treatment of each, the filter being well incinerated. If the precipitate has not the correct black-blue colour after a slight ignition, it is moistened with a little ammonia, dried, and again ignited. Organic matter is destroyed by previous ebullition in nitric acid or chromic acid. The molybdic precipitate is heated in a platinum crucible, preferably on platinum wire-gauze. The bottom of the crucible must not become red-hot, though the wire-gauze should display redness. At the same time this method of working allows the use of very small quantities of the average liquids. 20 grms. superphosphate were dissolved in 1 litre of water, and 10 c.c. of the solution were poured into 35 c.c. of the molybdic liquid, stirred for half an hour, and filtered cold; the precipitate washed, dried, heated, and weighed. It weighed:—

No. I.—0.9182 gm.

No. II.—0.9180 gm.

$0.9182 \times 4.018 = 3.6893276 \times 5 = 18.446$ p.c. P_2O_5 .

$0.9180 \times 4.018 = 3.6885240 \times 5 = 18.442$ "

After converting the molybdic precipitate into magnesium pyrophosphate, and ignition according to the usual method of Fresenius, there were obtained:—

No. III.—

$0.05763 \times 0.64 = 0.0368832 \times 500 = 18.4416$ p.c. P_2O_5 .

Twenty grms. of an arable soil, in which there had been obtained gravimetrically, according to the most trustworthy method, 0.140 per cent phosphoric acid, gave by the cold method, when treated with 10 per cent cold nitric acid, after elimination of silica, and calculated on 100 c.c. of the acid solution, (0.7009×0.04018) , in which therefore 0.028162 $P_2O_5 \times 5$ in 100 grms. of fine earth 0.14082 per cent P_2O_5 .—*Chemiker Zeitung*, vol. xix., No. 25.

A REVISION OF THE ATOMIC WEIGHT OF STRONTIUM.

FIRST PAPER: THE ANALYSIS OF STRONTIC BROMIDE.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 20).

Preparation of Materials.

Strontic Bromide.—Six different specimens of the salt were analysed, in order to establish the presence or absence of accidental impurities.

In the first place, 500 grms. of the purest strontic nitrate of commerce were dissolved in 2 litres of pure water, and four times in succession a cubic centimetre of pure sulphuric acid diluted with much water was added

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy*.

to the solution. Each time only a small amount of precipitate appeared at once, the rest appearing slowly. After waiting in each case three or four days, the clear liquid was decanted. No barium could be found even in the first precipitate of strontic sulphate; but it is true that the spectroscopic is not a very satisfactory means for the detection of barium under these circumstances. The acid solution of strontic nitrate, which had been thus almost if not quite freed from a possible trace of barium, was evaporated to small bulk, filtered from the precipitated strontic sulphate, and twice successively brought to crystallisation. Each mass of crystals was washed three times with alcohol upon the filter-pump, to free it from the mother-liquor, which might contain calcium or magnesium. After having been converted into pure carbonate by precipitation with ammonic carbonate and long-continued washing, the strontium was combined with bromine. For this purpose hydrobromic acid remaining from the barium work, obtained by repeated fractional distillation of the common acid, was used.

The strontic bromide was evaporated in a platinum dish. This was slightly attacked, bromine having been set free by a little occluded strontic nitrate in the carbonate. After evaporation to dryness the bromide was fused at a bright red heat in platinum. The alkaline solution of the fused cake was treated with hydric sulphide, filtered, acidified with hydrobromic acid, warmed, filtered from the platinic sulphide, boiled to free it from sulphuretted hydrogen, again filtered, and crystallised twice from water. The crystals were washed with alcohol, and the strontic bromide thus obtained is numbered I. below; it was used for the three preliminary experiments, as well as for Analysis 13.

The second sample of strontic bromide was prepared from similarly treated strontic nitrate which had been re-crystallised four times instead of twice. The nitrate was converted into oxide by ignition in a nickel crucible; and the dissolved residue was filtered to get rid of a small amount of nickel. Ammonic sulphhydrate gave no trace of colouration to a portion of the filtrate. Two re-crystallisations in a platinum bottle sufficed to free the strontic hydrate from a trace of undecomposed oxides of nitrogen, and the last crystals dissolved to form an absolutely clear solution in pure hydrobromic acid (see *Proc. Amer. Acad.*, xxviii., 17, bottom of page). The solution of strontic bromide was evaporated to crystallisation, the crystals were dehydrated, and the anhydrous salt was fused; finally, after solution, standing, and filtration, a fresh crop of crystals was obtained. This sample, labelled No. II., was used for Analysis 14.

Among several different methods for obtaining pure strontic salts, that recommended by Barthe and Falières (*Fourn. Chem. Soc.*, Abs., 1892, p. 1277; *Bull. Soc. Chim.*, [3], vii., 104) seemed to promise well, and accordingly the third preparation was based upon their work. The so-called "pure" strontic chloride of commerce was dissolved in water, treated with ammonic hydrate and a little carbonate, and filtered from the precipitate containing iron, aluminium, and so forth. To the filtrate was added an excess of sulphuric acid, and the precipitated strontic sulphate was thoroughly washed with dilute sulphuric acid and then with pure water, in the hope of freeing it from magnesium and calcium. When the wash water became neutral to methyl-orange the precipitate was treated with enough ammonic carbonate solution to convert about half of it into carbonate, and the mixed precipitate was then washed with water by decantation until only a very small constant trace of sulphuric acid (due to strontic sulphate) was found in the decantate. The carbonate was then decomposed by pure hydrochloric acid, and the solution was allowed to stand in a glass flask for nine months over the undecomposed sulphate, with occasional shaking. The strontic chloride was decanted, the sulphate was washed once with water, and the filtered decanted liquid was evaporated in a platinum dish until most of the free hydrochloric acid had been expelled. The dis-

solved residue was neutralised with ammonia, shaken with a little ammonic carbonate, and then filtered. To the greatly diluted filtrate was added an excess of pure ammonic carbonate, and the precipitate was washed until the wash-water was free from chlorine. The strontic carbonate was dissolved in nitric acid which had been twice distilled in platinum, and the nitrate was crystallised twice successively in a platinum dish. Each quantity of crystals was washed with small quantities of water and three or four additions of alcohol. The first mother-liquor, upon being fractionally precipitated by means of alcohol, showed distinct traces of calcium in the extreme solution; thus Barthe and Falières's method was not capable of freeing the substance wholly from calcium. The second mother-liquor showed no trace of calcium upon the most careful scrutiny.

200 grms. of the purest crystals, after having been dried at 130°, were dissolved in about a litre of the purest water and filtered into a large platinum dish, into which was passed first pure ammonia gas and then pure carbon dioxide through a platinum tube (see "Ammonic Carbonate"). The pure strontic carbonate was washed by decantation eight or ten times, dried on the steam-bath, and ignited in a double platinum crucible over a spirit-lamp.

Part of this carbonate was converted into bromide by means of the purest hydrobromic acid (prepared from pure baric bromide and re-distilled many times; see *Proc. Amer. Acad.*, xxviii., 17), and the product was digested for a long time with a considerable excess of carbonate. After filtration and evaporation the strontic bromide was fused in a platinum dish over the spirit-lamp; the salt being perfectly clear while liquid. The translucent cake was dissolved, allowed to stand, filtered, faintly acidified with hydrobromic acid, and crystallised twice from water. Each time the crystals were washed with the purest alcohol. The resulting bromide of strontium was used for Analyses 1, 2, 3, 5, 6, 7, 12, 15, 16, 17, and 18.

The next sample was prepared from the strontic carbonate which had been digested with the strontic bromide just described. It was dissolved in the purest hydrobromic acid, and purified much as before, except that the salt was fused twice with intermediate crystallisations, instead of only once. This fourth preparation was used for Analysis 9.

The fifth sample was made by the repeated crystallisation of the combined mother-liquors obtained from the four previous preparations. It was used for Analyses 4, 8, and 19.

The sixth preparation of strontic bromide was made from the strontic sulphate remaining from the third. This residue was treated with enough ammonic carbonate to convert all but about 20 grms. of the sulphate into carbonate. The washed strontic carbonate having been dissolved in a slight excess of hydrochloric acid, the residual sulphate was allowed to remain in the solution for a week. After filtration, evaporation to dryness in platinum, solution, a second filtration, treatment with a little ammonic hydrate and carbonate, and yet another filtration, the strontic chloride was converted into carbonate by means of purified ammonic carbonate (see "Ammonic Carbonate"). After a very complete washing the strontic carbonate was dissolved in pure nitric acid in a platinum dish. The nitrate was crystallised, dried at 150°, re-crystallised, washed with alcohol with the aid of the pump, dried, dissolved, and stirred with a little pure strontic carbonate for a week. The filtrate containing pure strontic nitrate was diluted, brought to boiling in a platinum dish, and poured in a fine stream into a boiling solution of pure ammonic oxalate (see "Ammonic Oxalate") also contained in platinum. The strontic oxalate was washed with the purest water upon the filter-pump, until no ammonia could be detected upon boiling the filtrate with sodic hydroxide. Nessler's reagent still showed a trace of ammonia; but since this could easily be expelled by ignition, and the precipitate was very hard to handle, the

washing was not carried further. After drying and powdering, the oxalate was converted into carbonate by ignition at a full red heat. The product was now ground in a mortar with an equivalent amount of pure ammoniac bromide (see "Ammoniac Bromide"), and the whole was gently ignited in a large platinum dish until no more ammonia was evolved. The 100 grms. of strontium bromide thus obtained formed a pure white translucent cake upon fusion in a large platinum crucible. The cake was dissolved in water, and the alkaline solution, after having been boiled for some time, was neutralised with sulphuric acid. The clear filtrate from the strontic sulphate was now evaporated to a volume of about 120 c.c., and diluted with 200 c.c. of the purest alcohol. The mixture was allowed to stand for a day, in order that the strontic sulphate and any trace of baric sulphate which might remain should be precipitated, and then filtered. After three successive crystallisations from water, the substance was used for Analysis 10; a further crop of crystals from the purest mother-liquor served for Analysis 11.

Considering the pains taken in the purification of even the least pure sample, it is not surprising that all of these samples gave quantitative results which proved them to be essentially identical.

Silver.—The preparation of pure silver has been repeatedly detailed. The most elaborate method described in the paper upon barium was used in the present case (*Proc. Amer. Acad.*, xxix., 64, 65). A few improvements were introduced, notably the purification of the sodic hydrate used for the reduction of the argentic chloride by means of a strong galvanic current, instead of by hydrogen sulphide. Little but iron was found in it, however. The final crystals of electrolytic silver were usually fused upon pure sugar charcoal or lime, in a reducing flame; once, however (for Analysis 10) the crystals contained in a lime boat within a stout porcelain tube were fused in a Sprengel vacuum by means of a Fletcher furnace. Two holes bored through the furnace at right angles to the flame entrance served to admit the tube. The heat was very gradually applied, and after the silver had been melted all the apertures of the furnace were closed and the tube was allowed to cool very slowly. A wide glass tube set into the porcelain tube on one end served as a convenient window for the observation of the fusion.

Ammoniac Carbonate.—Two varieties of ammoniac carbonate were used for the work just described. The first consisted of ordinary pure "ammoniac carbonate," which had been dissolved, treated with a small amount of a pure strontium salt, and filtered. This treatment undoubtedly removed any substance which could seriously interfere with the preliminary purifications for which this ammoniac carbonate was used. For the final stages of the purification of the strontium preparations, ammoniac carbonate was made by saturating the purest water in a platinum vessel with ammonia gas obtained by boiling the pure strong ammonia of commerce, and then passing into this saturated solution pure carbon dioxide. This latter gas was prepared by the action of dilute nitric acid on marble; it was purified by passing through washing flasks containing water and a meter of glass tube packed with moist beads. Upon delivering the gas into a Bunsen flame, no trace of calcium could be detected spectroscopically. Both gases were conducted into the solution through a platinum tube made for the purpose. The resulting ammoniac carbonate undoubtedly contained more or less of the amines common in ordinary ammonia, but it could not have contained a trace of non-volatile impurity capable of contaminating the strontic carbonate for whose preparation it was designed.

Ammoniac Oxalate.—This salt was made by neutralising pure ammonia water with pure oxalic acid, which had been still further purified by many re-crystallisations from hydrochloric acid and water. The ammoniac oxalate was crystallised twice in a platinum dish, the crystals being thoroughly washed each time. The salt was wholly free from chlorine.

Ammoniac Bromide was prepared in the usual fashion from ammonia prepared in platinum and bromine purified according to Stas. The reaction was naturally conducted in a flask of hard glass; but the crystallisation was carried on as usual in platinum. A slight excess of the pure white substance precipitated 3.97970 grms. of argentic bromide (fused, reduced to the vacuum standard) from a solution containing 2.28616 grms. of pure silver. From this experiment $\text{AgBr} : \text{Ag} = 100 : 57.4455$. Stas found 57.445, hence the purity of the ammoniac bromide is proved.

A very simple and convenient platinum condenser was used for the preparation work described above. The tube, almost a centimetre in diameter, and perhaps twenty-five centimetres in length, is bent, somewhere contracted near one end, and surrounded with a condenser jacket. It is easy to draw out the neck of a round-bottomed flask to fit outside of the conical end, and if the juncture is not absolutely tight a thin film of condensed liquid soon makes it so. If the glass neck be prolonged somewhat above the point of juncture, evaporation from this film is very slow. Of course pure filter paper may be used to tighten the joint if water is to be distilled. The apparatus has the great advantages of cheapness and transparency over the ordinary platinum still. All the hydrochloric, hydrobromic, sulphuric, and nitric acids, water, and alcohol used in the important stages of the work were distilled with the help of this contrivance.

Platinum vessels have been used wherever it was possible to use them in the work detailed above, although the fact is not always mentioned. They were cleaned in the usual fashion.

(To be continued.)

NOTE ON THE FORMATION OF CITRIC ACID BY THE OXIDATION OF CANE-SUGAR.

By ALFRED B. SEARLE and ARNOLD R. TANKARD.

IN the *CHEMICAL NEWS* (lxxii., p. 296) Dr. T. L. Phipson announces the formation of citric acid by the action of potassium permanganate, at 25° C., on cane-sugar in aqueous solution containing free sulphuric acid. We have carefully followed the directions given by Dr. Phipson, and, like him, obtained no precipitate on adding calcium chloride to the cold neutralised liquid resulting from the treatment with permanganate, but on boiling a copious white precipitate was thrown down.

The precipitate obtained by us differed from that described by Dr. Phipson in the fact that it consisted wholly of hydrated calcium sulphate. Thus, the precipitate, after washing with hot water and drying at 100° C., lost 20 per cent of water on ignition, and did not darken during the process. The residue was not alkaline to litmus, and did not effervesce with acid. It contained sulphate and calcium in the proportions required by the formula CaSO_4 .

When the precipitate produced by calcium chloride was treated with dilute sulphuric acid, and the filtered liquid concentrated somewhat, small but well-formed crystals were obtained; but analysis and microscopical examination showed that they also consisted entirely of hydrated calcium sulphate, $(\text{CaSO}_4 \cdot 2\text{H}_2\text{O})$.

On treatment with boiling acetic acid the precipitate dissolved somewhat, but the precipitate produced by neutralising this solution with ammonia and boiling consisted entirely of hydrated calcium sulphate.

In order to avoid any confusion from precipitation of calcium sulphate, we have also employed nitric acid instead of sulphuric acid for acidulating the cane-sugar solution. In this case we obtained no precipitate on addition of calcium chloride to the neutralised liquid, even

on boiling, showing that no citric acid had been formed by the treatment with permanganate.

We have also added potassium permanganate to a solution of sodium sulphite, acidulated with sulphuric acid, until the colour was no longer discharged. The clear liquid was neutralised by ammonia, and calcium chloride added. On boiling the liquid a copious white precipitate was thrown down, but this evidently could have contained no citrate.

We are reluctant to believe that so experienced a chemist as Dr. Phipson would mistake a precipitate of calcium sulphate for one of calcium citrate, but it is evident that the essential conditions must be described more precisely before other chemists can repeat Dr. Phipson's experiment with success.

67, Surrey Street, Sheffield.
July 13, 1895.

MONAZITE — A MINERAL CONTAINING HELIUM.

By ALBERT THORPE.

THE following figures represent the results of a recent analysis of a sample of monazite from North Carolina:—

Lanthanum oxide . . .	23.62
Cerium oxide . . .	25.98
Thorium oxide . . .	18.01
Phosphoric acid . . .	28.43
Tin oxide . . .	1.62
Manganous oxide . . .	1.33
Lime . . .	0.91
	99.90

As this mineral is known to contain helium, the above results of a careful analysis may be of interest to the readers of this journal. Due to the far-reaching researches of Ramsay, it is probable that chemists may find coronium and the primordial "material" in some of the rarer minerals, and the "lavas" ejected from active volcanoes.

ON CERTAIN PHENOMENA OBSERVED IN THE PRECIPITATION OF ANTIMONY FROM SOLUTIONS OF POTASSIUM ANTIMONYL TARTRATE.*

By J. H. LONG.

I HAVE elsewhere called attention to the behaviour of solutions of tartar emetic when treated with solutions of other salts (see *Am. Journ. Sci.*, O.S., 1889, and O.S., 1890), and with Mr. H. E. Sauer have determined the conditions of precipitation by carbonates, acetates, and phosphates (*J. Anal. Appl. Chem.*, March, 1891).

When to solutions of the antimony salt sulphates, chlorides, nitrates, and oxalates of the alkali metals are added no precipitation occurs, even with elevation of temperature. With carbonates, acetates, phosphates, borates, thiosulphates, sulphites, tungstates, and some other compounds, clear solutions can be made at a low temperature, but precipitation follows at a higher point. The precipitate, in nearly all cases, consists of hydrated antimony oxide, and its amount is a function of time, temperature, and amount of added salt.

With mixtures of the tartrate and sodium carbonate, for instance, it was found that in the cold, at the end of twenty-four hours, amounts were precipitated as shown in the following table. In each test 5 grms. of the tartrate were dissolved in 60 c.c. of warm water and cooled

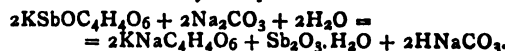
to 20°. Then different weights of pure sodium carbonate were dissolved in 35 c.c. of water; these solutions were added to the others and the mixtures were brought up to 100 c.c. They were allowed to stand until precipitation was complete, usually over night or longer. An aliquot part of the clear supernatant liquid was taken and the amount of antimony in solution determined. This was calculated to tartrate in the whole.

No. of experiment.	Na ₂ CO ₃ added. Grm.	KSbOC ₄ H ₄ O ₆ · ½H ₂ O left in solution. Per cent.
1.	0.1	99.93
2.	0.3	85.22
3.	0.5	70.36
4.	0.7	56.76
5.	0.9	40.87
6.	1.2	29.17
7.	1.5	13.94
8.	2.0	3.88

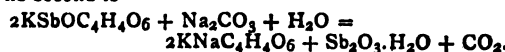
In another series of experiments the solutions of carbonate and tartrate were mixed as before at 20° and then brought to 100°, and maintained at this heat one hour. The precipitates formed immediately, and at the end of the hour were separated by filtration. The filtrates were tested for antimony remaining. The results are shown in the third column below.

No. of experiment.	Na ₂ CO ₃ added. Grm.	KSbOC ₄ H ₄ O ₆ · ½H ₂ O left in solution. Per cent.
9.	0.2	79.23
10.	0.5	46.70
11.	0.8	21.74
12.	1.1	8.69
13.	1.5	6.33
14.	2.0	4.42
15.	3.5	4.66
16.	5.0	4.74

On comparing the two tables it will be seen that at first the precipitation is much more rapid in hot solution than in cold, but that finally, with excess of carbonate, a more complete decomposition of the tartrate is effected in the cold solution. Two equations can be given, according to which the reaction may take place. The first of these is—

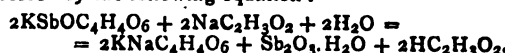


The second is—

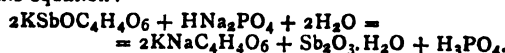


The first, probably, takes place in the cold solution, as no carbon dioxide escapes. The loss of carbon dioxide from the hot solution is less than called for by the equation, because an excess of neutral carbonate is present and the solutions are not actually boiled. In any case the precipitation is incomplete, and by addition of increased amounts of sodium carbonate, a condition is reached in which a part of the oxide at first thrown down appears to go into solution again.

Precipitation with sodium acetate takes place imperfectly in the cold, but by heat a stronger reaction follows. In both cases it was found that the results may be expressed by the following equation:—



With phosphates the experiments led to the conclusion that precipitation takes place in a manner represented by this equation:—



With cold solutions precipitation is very slow, but by heat an amount of the antimony oxide corresponding to 75 per cent of the tartrate originally in solution is obtained.

* *Journal of the American Chemical Society*, vol. xvii, No. 2.

I have since investigated the behaviour of several other salts as precipitants, with the results which follow.

Reaction with Sodium Biorate.

A very sharp reaction takes place between solutions of borax and tartar emetic, which was studied in the following manner. In the first series of experiments 5 grms. of the tartrate were dissolved for each test in 60 c.c. of water, the solutions being brought to 20°. To these were added definite weights of borax dissolved in 30 to 35 c.c. of water at the same temperature. The mixtures were made up to 100 c.c. exactly, and allowed to stand over night in a place with nearly constant temperature. In all cases a precipitate formed which was separated by filtration. The analysis of the precipitate showed it to have the same composition as that formed by the sodium carbonate; viz., $\text{Sb}_2\text{O}_3 \cdot \text{aq}$. On drying at a high temperature most of the water is lost, leaving practically Sb_2O_3 .

In each case the precipitate was separated by filtration, and the filtrate made up to 250 c.c. 25 c.c. of this was taken and precipitated by hydrogen sulphide, after addition of tartaric and hydrochloric acids in small amount. The precipitation was finished on a hot water-bath, and the precipitate collected on a Gooch filter, washed, dried at 120° and weighed. The sulphide was calculated to tartrate on the supposition that all the antimony in solution was left in the original form ($\text{Sb} = 120, \text{O} = 16$). The results obtained are shown by these figures:—

No. of experiment.	Borax added. Grm.	$\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ left in solution. Per cent.
1.	0.1	98.81
2.	0.2	94.74
3.	0.4	87.78
4.	0.8	74.98
5.	1.6	46.84
6.	3.2	3.31

In another series of tests the solutions containing the borax and tartrate were made up to 250 c.c. instead of to 100 c.c. They were allowed to stand, filtered, and treated as before, giving these results:—

No. of experiment.	Borax added. Grm.	$\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ left in solution. Per cent.
7.	0.1	100.00
8.	0.2	97.15
9.	0.4	89.05
10.	0.8	75.29
11.	1.6	49.09
12.	3.2	6.01
13.	6.4	2.03
14.	12.8	0.99

In a third set of experiments the liquid containing the borax and tartrate was diluted to 100 c.c. in a flask, as in the first set. The flask was closed with a perforated rubber stopper having a long glass tube attached, and then heated in boiling water one hour. The liquid was allowed to cool, was filtered, and the filtrate made up to 250 c.c. An aliquot part, on analysis, gave results which are shown below.

No. of experiment.	Borax added. Grm.	$\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ left in solution. Per cent.
15.	0.1	99.88
16.	0.2	95.37
17.	0.4	88.81
18.	0.8	74.78
19.	1.6	47.03
20.	3.2	3.96
21.	6.4	1.76

In these tables several things are immediately apparent. It appears that the precipitation is less perfect in hot solution than in cold, although for equal weights of

borax the differences are not great. It is seen also that the amounts precipitated are greater in the strongest solutions. These effects of temperature and concentration are far less marked, however, with borax precipitation than with that by the sodium carbonate.

With borax we have, in each case, a very regular rate of precipitation. By plating the weights of borax in the above table as abscissæ, and the amounts of tartrate left as ordinates, we obtain a curve which is almost a straight line.

It seems practically impossible to precipitate all the antimony by excess of borax, although the amount left in solution is much less than when sodium carbonate was used as the precipitant. Direct trials showed that the solubility of the antimonous oxide in excess of borax solution is very slight, but is a trifle greater in the excess of sodium carbonate. The solubility in the Rochelle salt solution formed in the latter case will not account for this difference, as will appear below.

In order to gain further insight into the reaction I measured the amount of rotation of polarised light in a number of solutions before and after the separation of the precipitate of antimonous oxide. Some exceedingly interesting results were obtained, a few of which will be explained in detail. I dissolved 5 grms. of the tartrate in 50 c.c. of hot water and added 3 grms. of borax in 25 c.c. of water, made up to 90 c.c., and heated half an hour in the water-bath. The solution was allowed to cool to 20° and made up to 100.5 c.c. (on account of volume of precipitate), and filtered through a dry filter. The filtrate was polarised in a 200 m.m. tube giving

$$\alpha_D = 3.596^\circ$$

Seventy-five c.c. of the filtrate, after the addition of a little hydrochloric and tartaric acids, was precipitated by hydrogen sulphide. The precipitate was collected, washed, and dried in the usual manner in the Gooch funnel. I found 0.119 gm. of the sulphide, corresponding to 0.312 gm. of $\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$, in the whole filtrate. 4.688 grms. had, therefore, been precipitated. From the outset it would naturally occur to one that the precipitation of antimonous oxide must be accompanied by the formation of sodium potassium tartrate, and that the polarisation effect observed must, in part, be due to this as well as to the potassium antimonyl tartrate left. I have elsewhere given the results of very accurate tests in which the rotation constants of these tartrates were determined by the use of the large Landolt-Lippich polarimeter with the 400 m.m. tube (*Am. Jour. Sci. and Arts, loc. cit.*) From these it appears that the rotation of 0.312 gm. of the $\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$, and 3.982 grms. of $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ (this latter corresponding to the tartar emetic decomposed) in 100 c.c. should not be over 2.6°. In the direct polarisation of the filtrate I found, as given above, 3.596°. It is evident, therefore, that something else must be present to modify the result.

It is well known that the presence of boric acid increases the rotation of tartrates in a marked degree, and this can be readily accounted for here if we assume that the reaction takes place according to the following equation:—



On applying tests for free boric acid its presence was readily shown. We have here apparently a reaction similar to those in which acetic and phosphoric acids are liberated from acetates and phosphates.

In the last experiment it was shown that antimony, corresponding to 0.312 gm. of the potassium antimonyl tartrate was still in solution, or that 4.688 grms. had been decomposed. To do this according to the above equation would require 2.697 grms. of crystallised borax, and would leave in solution 3.982 grms. of $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ and 1.751 grms. of H_3BO_3 . An excess of 0.303 gm. of

borax would be left in solution. To test the correctness of this view I prepared a solution containing in 100 c.c., at 20°—

0.312 grm. of $\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$,
3.982 grms. of $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$,
1.751 grms. of H_3BO_3 ,
0.303 grm. of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$.

This solution was polarised in the 200 m.m. tube, and gave—

$$\alpha_D = 3.590^\circ,$$

which agrees very well with the result of the first experiment. Another solution, containing in 100 c.c., at 20°—

0.150 grm. of $\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$,
4.119 grms. of $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$,
1.811 grms. of H_3BO_3 ,

gave $\alpha_D = 3.661^\circ$. While boric acid increases the rotation of tartrates and tartaric acid, I have elsewhere shown that borax decreases the rotation of Rochelle salt slightly. The equation probably represents the facts properly.

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

INTERNATIONAL CATALOGUE COMMITTEE.

The following Report was presented to the President and Council on July 5th; the recommendations contained in it were approved of, and the Secretary was directed to send copies to the several correspondents, and to certain scientific papers:—

Report.

At the first meeting of this Committee (February 8, 1894) the Memorial to the President and Council (July, 1893) which led to the appointment of the Committee, and the Minute of Council of December 7, 1893, appointing the Committee, having been read, it was resolved to request the President and Council to authorise the Committee to enter directly into communication with societies, institutions, &c., in this country and abroad, with reference to the preparation, by international co-operation, of complete subject and authors' catalogues of scientific literature.

Subsequently a draft circular letter was prepared, which, on February 22, 1894, received the approval of the President and Council, who also authorised its issue.

This letter was sent to 207 societies and institutions selected from the exchange list of the Royal Society, and to a few others. It was also sent to the Directors of a number of Observatories and of Government geological surveys, to the Foreign Members of the Royal Society, as well as to those of the following Societies:—Chemical, Geological, Physical, Royal Astronomical, Linnean, Royal Microscopical, Entomological, Zoological, Physiological, and Mineralogical, and of the Anthropological Institute. A special letter was addressed to the Smithsonian Institution.

More than a hundred replies to the letter have been received; several of these are reports of committees specially appointed to consider the suggestions put forward by the Royal Society. A list of answers received up to December, 1894, with brief excerpts from the more suggestive, was issued to members of the Committee early in this year. It should, however, be added that from some important institutions no answer has as yet been received.

It may be said at the outset that in no single case is any doubt expressed as to the extreme value of the work contemplated, and that only two or three correspondents question whether it be possible to carry out such a work.

It is a great gratification to the Committee that the matter has been taken up in a most cordial manner by the Smithsonian Institution, the Secretary of which, in his reply, refers to the desirability of a catalogue of the kind suggested as being so obvious that the work commends itself at once. The importance of having complete subject catalogues, and not mere transcripts of titles, is also generally recognised.

Some bodies and individuals take the matter up very warmly, and urge that steps be taken forthwith to put the scheme into action, this being especially true of the replies received from the United States; others, while giving a general approval, dwell upon the difficulties of carrying out the suggestions put forward; and others, again, ask for more details before committing themselves to any answer which may seem to entail future responsibility, especially of a financial character.

Incidentally it may be pointed out as very noteworthy that over and over again reference is made to the great value of the Royal Society's "Catalogue of Scientific Papers." There is abundant evidence that considerable use is made of this on the Continent of Europe. And it is clear that a proposal to carry out a more comprehensive scheme initially under the direction of the Royal Society of London is likely to meet with general approval, owing to the fact that the Society is credited with having already carried out the most comprehensive work of the kind yet attempted. Indeed, the Academy of Natural Sciences of Philadelphia, U.S.A., directly advocates the establishment of a central bureau under the Royal Society; and several others more or less clearly imply that they would favour such a course.

Over and over again, it is stated that the production by international co-operation of a catalogue such as is contemplated is not only desirable, but practicable. The Americans, who, as already stated, are the most enthusiastic supporters of the scheme, especially dwell on the importance of early action being taken. Prof. Bowditch, of Harvard University, in particular, points out that if the Royal Society of London wish to guide the enterprise, it ought to announce its views and put forward a comprehensive scheme with the least possible delay. It may be added here that he also urges that in determining the scope of the catalogue a very wide interpretation should be given to the word "Science."

No very precise information as to the best mode of putting the scheme into operation is to be gathered from the replies as a whole.

It is generally agreed that the enterprise should be an international one. Many think that international financial support should and would be accorded to it, but no method of securing this is indicated; others express the view that the cost may be met by subscriptions from societies, libraries, booksellers, and individuals, without Government aid; and this is perhaps, on the whole, the prevailing feeling among those who have discussed the matter from a financial point of view. But in no case is any attempt made to form any exact estimate of the cost.

A number of scientific bodies and institutions express themselves prepared to work in such a cause. The Secretary of the Smithsonian Institution suggests that, as the Institution receives all the serials and independent works published in America, a branch-office might be established there, and that it is not impossible that a sum of money might be given yearly in aid. The Royal Danish Academy is willing to render as much assistance as possible. It would charge an official of one of the Danish chief libraries in receipt of all Danish publications with the task of editing slips, and would defray the cost of this work. The Société des Sciences of Helsingfors would furnish the Central Office with information as to the scientific work done in Finland. The Kongl. Vetenskaps Akademi of Stockholm would organise a Committee for Sweden.

As regards language, there appears to be more unanimity than could have been expected. Over and over again

the opinion is expressed that English should be the language of the subject catalogue. Frequent reference is made to the importance of quoting titles in the original language, although some suggest that this should be done only in the case of those published in English, French, or German, and perhaps Italian.

Some form of card catalogue appears to be generally favoured, especially in America, as the basis of the scheme; the Committee of Harvard University, whose reply is very full, in particular discuss this point in detail.

In an interview with the Committee in March last, Prof. Agassiz spoke very warmly in favour of the scheme, and of the support which it would meet with in the United States, especially from libraries. As others have done, he strongly urged that the co-operation of booksellers and authors should be secured. Prof. Agassiz also expressed the view that the regular issue to libraries and scientific workers from the central office of cards or slips which would afford the material for the construction of card catalogues would form an important source of income, at all events in his country.

From various sides it is urged that an International Congress should be held to discuss plans. This is advocated as a first step in a reply received from the Königl. Gesellschaft der Wissenschaften in Göttingen, a reply to which, not only as regards this point, but also in respect to the whole matter, the Committee attach very great weight, since it embodies in an official form views arrived at by the Academies of Vienna and Munich, and by the scientific societies of Leipzig and Göttingen, who have considered the matter in common. Prof. Agassiz strongly urged the calling of a Conference; and, among others who share this view, Dr. Gill, of the Cape Observatory, in his letter particularly dwells on the great value of such meetings as the means of securing unanimity of action.

Such being the tenor of the correspondence, your Committee are convinced that initial steps of a definite nature in furtherance of the scheme ought now to be taken.

They accordingly request the President and Council to take measures with the view of calling together, in July of next year (1896), an International Conference, at which representatives of the several nations engaged in scientific work should be invited to attend, with the view of discussing and settling a detailed scheme for the production by international co-operation of complete authors' and subject catalogues of scientific literature.

London will probably be found the best place in which to hold such a Conference. It may be desirable to summon the representatives of the different countries through their respective Governments, and it will obviously be necessary that a detailed scheme be prepared, to serve as a basis for discussion at the Conference. These and other points will require much consideration before any action at all can be taken; meanwhile it is desirable that a beginning should be made during the autumn, before the winter session of the Society. The Committee therefore recommend that the President and Council should give the Committee (which includes the President and Officers) executive powers in order that they may take, in the name of the Society, such steps as they may think desirable with the view of calling together the above-mentioned Conference.

Determination of Sulphur in the Leads of Commerce and in Work-lead.—W. Hampe (*Chemiker Zeit.*).

—The author describes two methods:—(a) Combustion of the specimen in a current of dry chlorine, and employs two receivers filled with water containing hydrochloric acid. (b) The oxidation of the lead is effected by means of melting saltpetre, and the sulphuric acid formed is determined. The reagents must be very carefully tested for sulphuric acid. Hampe's results place it beyond doubt that copper may contain copper semi-sulphide even in presence of oxygen.

NOTICES OF BOOKS.

The Manufacture of Explosives. A Theoretical and Practical Treatise on the History, the Physical and Chemical Properties, and the Manufacture of Explosives. By OSCAR GUTTMANN, Assoc. M. Inst. C.E., F.I.C., Member of the Societies of Civil Engineers and Architects of Vienna and Budapest, Correspondent of the Imperial Royal Geological Institution of Austria, &c. In Two Volumes, 8vo. Vol. I., pp. 348; Vol. II., pp. 444. London: Whittaker and Co. 1895.

THE author of this thorough-going work makes in his Preface a somewhat alarming statement. The book, he tells us, "is written for manufacturers and experts alone, and anarchists and such like will find nothing new in it." This sentence is certainly open to the construction that anarchists, dynamitards, &c., are, to say the least, fully equal to manufacturers and experts in their knowledge of high explosives. If this is true—and we are not in a position to contravert it—"pity 't is 't is true."

The first subject taken up is that of new materials. Here it is not without interest to note that diversities of opinion prevail concerning the best method of preparation, even in case of so anciently known a substance as charcoal. Another interesting fact is the case of a workman secretly drinking about half a pint of glycerin every day, because the burning in the stomach gave him the same sensation as brandy. This fact may throw a light upon the unaccountable disappearance of glycerin sometimes complained of in print- and colour-works.

The preparation of nitric acid for the manufacture of explosives is given in detail. The sale of this acid by specific gravity is shown to be untrustworthy, especially if the scale of Baumé is used, since "an exact definition of this hydrometric scale does not exist." It is remarked that it is becoming more and more the custom to designate commercial nitric acid in a rational manner, namely, by the percentage of pure nitric monohydrate which it contains.

The general properties of explosives are discussed in the second chapter. They are classified by Colonel Hess into low or direct explosives (ordinary gunpowder being the type), and high or indirect explosives (the type gun-cotton), the highest effect of which is obtained by means of an intermediate agent.

The views of Berthelot, and their criticism by Sir F. Abel and Nobel, are given, and in addition we have certain fantastic methods for increasing the force of gunpowder, dating back to the year 1563. Tables are given showing the composition of gunpowder at different times and in different countries. The manufacture and the properties of prismatic and compressed powders are described and illustrated. There are also a number of powders in which potassium nitrate is partially or entirely replaced by other nitrates, or by potassium chlorate. The number of powders in which some other substance is substituted for charcoal is wonderful, though in most cases with no definite advantage.

The points to which attention is directed in the examination of powders are external condition, solidity of grain, size of grain, density as ascertained with a variety of densimeters, hygroscopic properties, and determination of moisture. Then follows the determination of the various ingredients.

Next we have an examination of what are called the mechanical properties of the powder, viz., the inflammability (it being shown, according to the experiments of Dr. Dupré, that there is scarcely any explosive which will not explode if spread in a thin layer on a wooden floor, and struck a glancing blow with, e.g., a broom-handle), rapidity of ignition, combustion, and products of combustion.

The second volume opens with the manufacture of gun-cotton, and its treatment from every point of view.

It is followed by picric acid and the picrates. Picric acid re-melted seems to be the much-vaunted "melinite" of the French, known in Britain as "lyddite." Picric acid in contact with the metal walls of projectiles seems to undergo changes which interfere with its stability. In its place sodium, potassium, and ammonium picrates have been proposed. A mixture of 432 parts of ammonium picrate with 568 parts of potassium nitrate is under examination on behalf of the French Government.

Trinitro-cresol is used in France, under the name of cresylite, for filling shells and torpedoes, and is ignited by means of a gun-cotton primer.

In Austria the ammonium salt of trinitro-cresol is used under the name of "ecrasite," and is said to be twice as powerful as dynamite.

Blasting-gelatin is a solution of soluble gun cotton in nitroglycerin, and has the advantage of being less susceptible to mechanical shocks than dynamite; but its manufacture is not at all easy.

Cordite, which has recently obtained political notoriety, is made by adding 58 parts nitroglycerin to 37 parts gun-cotton and 5 parts of vaselin. The accidents with this compound which have occurred at Waltham Abbey do not seem due to any defect in the composition.

A point which does not seem to have been made sufficiently prominent concerns the propagation of the shock from explosions of the higher explosives. This takes place not merely through the air, but through the earth. Thus, at the gun-cotton explosion at Stowmarket, the windows of houses at the distance of a mile from the magazine, and looking in the opposite direction, were seen falling out of their frames *before* the noise of the explosion had reached the spot. Hence belts of trees, traverses of earth, &c., are no complete protection against the effects of explosions.

This work commends itself most strongly to all manufacturers and users of explosives, and not less to experts, who may be called on to examine the causes and results of disasters of the kind in question.

Petroleum: its Development and Uses. By R. NELSON BOYD, Member of the Institution of Civil Engineers. Whittaker and Co. 1895. Crown 8vo., pp. 85.

We have here a most useful manual of the origin, composition, properties, and uses of mineral oils. On many of these points consumers and dealers are lamentably ignorant—an ignorance greatly to be regretted concerning an article so valuable, if rightly used, so perilous in careless hands, and introduced into trade in such enormous quantities. We learn here that the imports of "petroleum oils" into the United Kingdom in 1893 reached a total of 155,126,667 gallons, whilst in addition 20,000,000 gallons of oils are obtained from the shales of Scotland.

The number of accidents due to petroleum lamps badly constructed or foolishly managed is very serious, and if we consider that as much as 4,000,000 gallons have been stored at one time at a single wharf in London there is always a possibility of a conflagration on a gigantic scale. Concerning its storage and safe-keeping British law is singularly lax. There is no regulation as regards the quantities which may be stored at or near one place; nor, apparently, as to the construction and security of the magazines. It is indeed enacted that the oil kept for sale must have a flashing-point of 73° F. close test. It is generally admitted by practical men that this point is too low for public safety. In Russia the standard fixed is 82°; in India, 110°, on account of the high temperature to which the oil may be exposed. Germany ventures upon a lower standard than our own, i.e., 70°. If this figure is really degrees Fahrenheit, and not Centigrade, we cannot help feeling surprised.

A very important point to which the author invites consideration is the supply of petroleum. At present our imports are almost exclusively derived from the United States and from Russia. There is here an element of

danger, since the consumer may suddenly find the cost price raised by dint of combinations. It is therefore very important that other sources should be sought for, and, if practicable developed. Mr. Boyd mentions here Mexico, Venezuela, and the La Plata regions. In addition, there is Burmah, Java, and Borneo. The use of heavy mineral oils and of petroleum residues for heating engines is a sober reality which deserves to be kept in view as a countercheck to the manoeuvres of the coal merchants and the unions of the coal miners.

The origin of petroleum is duly discussed. The theories of its inorganic origin, as advocated by Professors Berthelot and Mendeleeff, are now generally laid aside in favour of the view of Bischoff, that all the mineral hydrocarbons are produced by the decomposition of organic matter, of vegetable origin in Pennsylvania, and of animal origin in Canada. It is now concluded to have been formed, not by destructive distillation, but at the normal temperatures of the earth.

The fact that petroleum is often accompanied by brine is not fully explained. The heaviest mineral oil here mentioned is that of Baku (sp. gr. 0.954), and the lightest that of Pennsylvania (0.730).

This excellent little work is furnished with appendices showing the percentages of theoretical heat converted into useful work by different motors; the flashing-points of mineral oils permitted in different countries; the suggestions as to the construction and management of petroleum lamps issued by the London County Council, but not extending to "benzoline" lamps; thermic values of different mineral oils; and import duties on petroleum in foreign countries and throughout the British Empire. We find that, except the home kingdoms and India, mineral oils are nowhere admitted free.

Chemistry, Organic and Inorganic, with Experiments. By CHARLES LOUDON BLOXAM. Eighth Edition. Rewritten and Revised by J. MILLAR THOMPSON, Professor of Chemistry, King's College, London, and ARTHUR G. BLOXAM, Head of the Chemistry Department, the Goldsmiths' Institute, New Cross, London. London: J. and A. Churchill.

THE work before us, which has now reached its eighth edition, is an excellent specimen of what we may call the intermediate type of chemical treatises. It does not aspire to the encyclopædic character of such works as those of Roscoe and Schorlemmer, Watts, and others, but, on the other hand, it avoids the bald fragmentary character of the manuals written in accordance with some syllabus.

The subject-matter has been modified in accordance with the present state of science. Argon and helium have been duly noticed, as far as their properties are already determined. Hydrazine and its derivatives are considered on p. 16. The periodic classification of the elements is expounded; so, likewise, are the fundamental principles of thermo-chemistry, the static method of measuring chemical energy, mass action, the kinetic theory of gases, and dissociation. Such matter, the theoretical aspect of the science, has been placed after the consideration of the non-metallic elements.

After each group of metals there follows a general review of its constituents.

In organic chemistry, the usual division of the substances discussed into fatty and aromatic derivatives has not been retained.

Under the physical properties of organic compounds we find mention of the absorption-spectra, which are thus mentioned detached from the general view of spectrum analysis on p. 303.

The respective applications of chemistry, inorganic and organic, are very fairly explained as far as the bulk of the work can allow.

The rare earths are not ignored, as is too frequently

the case, though the elementary character of some of them is not regarded as fully established.

A few oversights cannot escape notice. Thus, in speaking of the Stephenson and Davy safety-lamps—recognised as not absolutely trustworthy—it is mentioned that a Davy lamp may show as little as 0.25 per cent of fire-damp, whilst on the next page (p. 109) we find it observed that "the Davy lamp will not indicate less than 2 per cent."

The sources of diamond are said to be Golconda, Borneo, and Brazil, though the two former deposits are nearly exhausted, and all three together yield a much smaller supply than does South Africa.

Absinthe is mentioned without any due condemnation of its use.

Passing over, however, such trifling omissions, we must pronounce Bloxam's work to be deserving of the full confidence of teachers and students.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Zeitschrift für Analytische Chemie.
Vol. xxxiii., Part 5.

New Apparatus for Evolving Sulphuretted Hydrogen.—F. W. Küster (*Journ. Prakt. Chemie*).—This paper requires the accompanying cut.

Vacuum Desiccation Apparatus.—L. Storch (*Ber. Osterr. G. and Zeit. Angew. Chemie*).—This paper cannot be intelligibly reproduced without the illustration.

New Apparatus for Extraction.—H. W. Wiley.—*Journ. Anal. and Appl. Chemistry*.

Trustworthy Still-heads.—Max Müller and also L. L. de Koninck.

Determination of Ammonia by Distillation.—Fr. Stolba (*Chemiker Zeitung*).

Washing-bottle for Gases.—J. Habermann (*Zeit. Angew. Chemie*).

Absorption Apparatus for Determining Sulphur in Iron and Steel.—E. M. (*Stahl und Eisen*).

Fixed Absorption Receiver for Permanent Use.—Kenneth Mackenzie (*Journ. Anal. and Appl. Chemistry*).—All these papers require the accompanying illustrations.

Automatic Safety Clamp for the Rider of Balances.—O. A. Richter (a circular issued by the author).—The arrangement is a claw which secures the rider and rises automatically if it has to be taken off or put on.

Use of Glycerin as a Heating Liquid in Soxhlet's Drying Apparatus.—Karl Seubert (*Zeit. Angew. Chem.*).—The author shows that if a solution of common salt is used as a heating liquid, leakages appear, even after a short use. This is a consequence of the galvanic contact of the different metals which occasions decomposition of the sodium chloride and solution of the soldering. Glycerin is free from these disadvantages. The author uses it in a 60 per cent solution, boiling at 108–109°, when the escaping current of air indicates 104°.

Safety Gas Jet.—F. Manoschek (*Dingler's Polytech. Journal*, cclxxxiv., 43).—If the flame is extinguished from any cause the flow of gas is arrested.

New Form of Clay Triangle for supporting Platinum Crucibles.—J. B. Coleman.—From the *Journal of the Society of Chemical Industry*.

Indicators for Use in Titration with Normal Solutions of Sulphide.—P. Williams.—From the *CHEMICAL NEWS*.

Preparation of Zinc free from Arsenic.—II. Leacœur.—From the *Comptes Rendus*.

Occurrence of Ammonia in Zinc Powder.—P. Robineau and G. Rollin.—This is said to be partially soluble, and can be recognised by treatment with hot water, and tested with Nessler's reagent. In part it exists in combination, and can be liberated by boiling with soda-lye. A product free from ammonia can be obtained by boiling and washing with dilute sulphuric acid (1:100). The formation of ammonia ensues on the oxidation of the finest zinc powder in contact with air.

Occurrence of Sodium Cyanide in Potassium Cyanide.—T. B. Stillman.—From the *Journal of Analytical and Applied Chemistry*.

Detection and Determination of Lead in Tartaric and Citric Acids.—R. Warrington.—From the *Journal of the Society of Chemical Industry*.

Determination of Chlorine in Commercial Iodine.—F. Ullzer and A. Friedrich.—*Mitt. k. k. Gewerbe Museum and Journal of the Society of Chemical Industry*.

Detection of Iodic Acid in Nitric Acid.—Loof (*Apotheker Zeit.* and *Rep. Chem. Zeitung*).—To 5 c.c. of the official acid the author adds 0.1 grm. calcium and sodium hypophosphite. If iodic acid is present a colouration appears in a few minutes, and can be made more distinct by means of chloroform.

Preparation of Pure Concentrated Hydrobromic Acid in Quantity.—E. Léger.—From the *Comptes Rendus*.

Volatility of Stannic Chloride.—T. M. Drown and G. F. Eldridge.—From the *Technological Quarterly*.

Presence of Arsenic and Antimony in Ores of the Upper Harz.—W. Hampe (*Chemiker Zeitung*).—Of interest chiefly to chemists and metallurgists of the Harz district.

Attraction of Water by Iodine and Determination of Water in Iodine.—C. Meinecke.—*Chemiker Zeitung*.

Detection and Determination of Alkyl combined with Nitrogen.—J. Herzig and H. Meyer.—The authors observed that the alkyl-iodine derivatives of pyridin and quinolin on heating were decomposed into the bases and the iod-alkyls, and determine the latter according to Zeisel's method. The decomposition is nearly quantitative, and the quantity of alkyl found differs from the calculated amount only by 0.8 per cent.

Separation of Volatile Fatty Acids.—M. Wechsler (*Monatshefte*).—Liebig found that on the partial neutralisation of a mixture of volatile acids and subsequent distillation, the acid with the higher proportion of carbon passed over first into the distillate, whilst that with the lower proportion of carbon was left behind as a salt. Wechsler has examined in this manner mixtures of formic, acetic, propionic, butyric, isobutyric, isovalerianic, and capronic acids. With one exception (the separation of butyric and isovalerianic acids), the first fraction always contained the pure acid with the higher proportion of carbon, whilst the constituent of the last fraction was the acid poorer in carbon.

Simultaneous Determination of Carbon and Nitrogen.—Felix Klingemann.—The author uses the process proposed by Frankland for the determination of nitrogen.

Determination of Nitrogen in Organic Substances.—A. Petit and L. Moufet.—From the *Journ. de Pharmacie and Journal of the Chemical Society*.

Determination of Nitrogen in Nitrates and in Admixture with Organic Nitrogen Compounds.—V. Schenke.—*Chemiker Zeitung*.

Determination of Glycerin.—S. Salvatori (*Stas. Sper. Agrar. and Journ. Chem. Soc.*).

Atomic Weight of Palladium.—E. H. Keiser and Mary B. Breed (*American Chemical Journal*).—The result obtained was Pd = 106.246.

Determination of Solubility of different Salts.—H. Landau (*Monatshefte*).—The author proceeds in the same manner as Deszathy, and gives his results in the form of a table.

Determination of Nitrogen in Organic Nitro-compounds, e.g., Nitro-glycerin.—P. Rubtsoff.—*J. Russ. Chem. Soc. and Journ. Chem. Soc.*

Determination of the Solubility of Barium and Calcium Butyrate.—A. Deszathy (*Monatshefte*).—This paper requires the accompanying illustration showing the author's apparatus.

Action of Sodium upon Water.—M. Rosenfeld (*Journal für Prakt. Chemie*).—Concerning the explosion which occurs under certain circumstances when sodium acts upon water, the author arrives at a conclusion antagonistic to previous conjectures. It was formerly supposed that peroxide was formed, and induced explosion by the development of oxygen. Proceeding on this view, Rosenfeld thought that large quantities of detonating gas might be obtained by passing watery vapour over sodium without the occurrence of explosion. No explosion occurred; but no trace of oxygen accompanied the hydrogen escaping. He considers that "sodium, in its action upon water, whether in open vessels or in those with a water-joint, is dissipated from the interior outwards, as in the phenomenon of spitting; the centre of the explosion lies in the interior of the metal, and the probable cause of the explosion is not the formation of detonating gas, but of a sodium hydride which is suddenly decomposed. The author deduces from his experiment a new method of preparing caustic soda and hydrogen. Sodium is placed in an iron pan, which can be closed with a lid, and watery vapour is introduced. If the access of watery vapour is cut off when the development of hydrogen ceases, we obtain solid caustic soda mixed with finely divided iron. Rosenfeld considers that there is first formed a sodium-iron alloy, which is then decomposed with the liberation of iron. Vessels of silver are also attacked.

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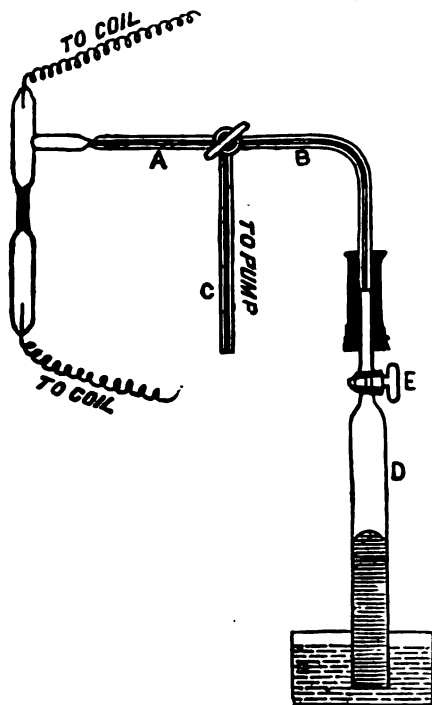
VOL. LXXII., No. 1861.

A METHOD OF TRANSFERRING GASES TO VACUUM-TUBES FOR SPECTROSCOPIC EXAMINATION.

By JAMES YOUNG, A.R.C.S., F.C.S., and
CHARLES R. DARLING, Wh.Sc., A.R.C.S. (Ireland).

WHILE engaged in an examination of the gases evolved by certain minerals, we found it necessary to devise a method of filling vacuum-tubes, using small quantities of gas, so as to recover all excess. The subjoined sketch shows the method adopted, and which we found to be more convenient than any other method we have tried.

A three-way capillary tap has one of its arms, B, bent at right angles. The tube D, containing the gas to be admitted over mercury, and possessing a plain tap, E, is connected to B by means of a mercury joint. Both taps must be perfectly vacuum-tight. The arm C is connected with the Sprengel or other pump, whilst the arm A is fused to the side-piece of the vacuum tube, which latter



is made of sufficient length to allow of convenient fusion. After joining to A, the side-piece is drawn out so that it may be readily sealed off after filling. The operation is then conducted as follows:—The three-way tap is turned so as to connect A and C, and pumping continued until as good a vacuum as possible is obtained. The tap E being closed, B and C are then connected, and the space between the two taps pumped free of air. The tap is now turned so as to connect A and B, and the tap E turned on, so as to admit a little of the gas into the vacuum tube. The arms A and C are again connected, and the excess of gas pumped out and collected over mercury at the bottom of the fall-tube, all loss being thus avoided. This process

is repeated two or three times to wash out the tube. The tubes may be sparked *in situ*, so that the pumping may be discontinued at any desired moment, and the tube sealed off.

We may mention that in a specimen of samarskite examined the residual gas obtained, after exploding with oxygen (to remove hydrogen and a hydrocarbon present), absorbing with potash, and removing excess of oxygen with alkaline pyrogallol, was found to be pure nitrogen. This was mixed with oxygen, and sparked for a considerable time over potash. There was a steady diminution of volume during the sparking; but at no period could any trace of helium be detected spectroscopically.

Whilst sparking the tubes with a strong current, with a fairly high vacuum, we obtained brilliant mirrors of platinum deposited on the sides of the tube adjacent to the platinum electrodes. This was particularly the case with those containing nitrogen, and when several strands of thin platinum wire twisted together were used as electrodes. With a single piece of thick wire as electrode, only a slight blackening was obtained. With hydrogen and oxygen, using the same current, there was only a very slight deposit in all cases. In the nitrogen tubes, when the deposit attained a certain density, the current flashed across radially from the electrodes, and after a time began to eat away the mirror from the edges, re-depositing a portion of it on the walls of the tube at the dark spaces. At the moment when the mirror began to conduct, a brilliant yellowish-green fluorescence was observed in the glass, which was scarcely visible previously. We have also noticed the phenomenon mentioned by Prof. Ramsay, viz., that with the deposition of the mirrors in nitrogen tubes the gas appears to be carried down by the platinum, a very high vacuum being in some cases obtained, which refused to allow the passage of the current.

Chemical Laboratory, Royal Military Academy,
Woolwich, July 16, 1895.

THE DETECTION OF SULPHATES, SULPHITES, AND THIOSULPHATES, IN PRESENCE OF EACH OTHER.

By R. GREIG SMITH, B.Sc.

THE separation of the acids has long been recognised as a matter of great difficulty by chemists and uncertainty by students, and it is with the intention of simplifying the detection of the commonly-occurring sulphur acids that the following method is given. Though it may not be altogether new, the process does not appear to be completely given in text-books on qualitative analysis.

Preliminary testing will probably have indicated the presence of thiosulphate, in which case a dilute solution of the substances under examination must be employed, or a decomposition of the thiosulphuric acid into sulphur and sulphuric acid will speedily take place. Barium chloride in excess is added, together with a good quantity of ammonium chloride, which, like many salts of ammonium, potassium, and calcium, acts as a flocculant or coagulant, and facilitates the filtration of the barium sulphate. Hydrochloric acid is next added, drop by drop, until it is evident that there is no further solution of barium sulphite and thiosulphate, and that only the sulphate remains undissolved; the solution is then filtered through a moistened double filter-paper, which should be free from "pin-holes."

The filtrate will probably be clear; but if not it should be returned to the filter for a second filtration. When too much thiosulphuric acid is present, the clear filtrate will visibly become clouded, or from being whitish will become more opaque: if this occurs the solution should be thrown out, and a fresh portion made more dilute. A solution of iodine is added to half of the filtrate until the colour is

of a permanent yellow tinge; a white precipitate indicates the presence of a sulphite which has been oxidised by the iodine to sulphate. In the absence of a decided precipitate, traces of sulphite may be readily detected by comparing the treated and the untreated halves of the filtrate—a procedure which very often saves a good deal of time, as it is unnecessary to wait until a clear filtrate is obtained. The two halves are mixed, and if the yellow colour disappears more iodine is added; the solution is filtered, and the filtrate divided into two halves as before. With a slight turbidity filtration may be omitted. Bromine water is added to one of the halves when any thiosulphate in the original solution shows itself as a white precipitate of barium sulphate, readily seen on comparing the two test-tubes. The thiosulphate is by the iodine converted to tetrathionate, which is oxidised by the bromine water to sulphate. Hydrosulphuric acid would interfere with these reactions, and ought to be eliminated by bubbling carbon dioxide through the solution until the gas escaping from the tube no longer darkens lead-paper.

Durham College of Science,
Newcastle-upon-Tyne.

THE PRODUCTION OF CYANIDES,

By H. N. WARREN, Research Analyst.

SINCE the establishment of the cyanide process for the separation of gold from its ores, the race for the production of that compound, in quantity and at cheap rates, has been almost as keen as were the previous attempts to reduce the alluvial deposits, and thus place upon the market the aluminium of to-day. Potassium nitrate, KNO_3 , has long been experimented with in the hopes of replacing the oxygen equivalent by carbon, and by so doing produce KCN ; but the large percentage of oxygen which is in every case set free at once determines the destruction of any cyanides thus formed, although traces of cyanides are always observed to be present after the partial reduction of commercial nitrates by means of carbon, owing to the secondary action of the ammonia thus formed, due to the moisture present.

Rochelle salt, mixed with a quarter of its weight of potassium nitrite, KNO_2 , and ignited, has given 5 per cent as the highest yield of cyanide obtainable, while most hydrated carbonaceous substances yield a still lower per cent. Anhydrous sodium acetate, in admixture with a nitrite, has yielded as much as 30 per cent of alkaline cyanide; whilst in a more recent experiment a mixture of 4 parts of wheaten flour to 1 part of nitrate, and the whole thoroughly mixed with 3 of magnesia and compressed into blocks, yielded, after ignition, from a varying percentage up to 15 per cent of cyanide. The production of sulphocyanides and the reduction of the same by means of lime and carbon, have on several occasions given valuable results in accordance with the following equation:—



but at other times, in consequence probably of the difficulty in regulating the temperature, has resulted in the formation of worthless substitutes.

On returning to the old method for the production of cyanides, by the incineration of nitrogen compounds, a valuable addition will be found in the use of lime or barium oxide; probably both the barium and calcium cyanides are more readily formed than alkaline cyanides; and in lixiviation, in contact with the alkaline carbonates present, they at once form alkaline cyanides and earthy carbonates or ferrocyanides, as arranged for.

Again, potassium and sodium cyanide together are much easier to produce than either separate, fusing at a much lower temperature, and containing more cyanogen, in consequence of the difference in the equivalent of sodium

when compared with potassium. A mixture of equal weights of the two alkalis reacts well in every respect, and yields good results.

Liverpool Research Laboratory,
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THE DETERMINATION OF URIC ACID, AND OF THE SO-CALLED XANTHIN-SUBSTANCES IN URINE.

By F. HOFMEISTER.

THE precipitate obtained, according to Salkowski-Ludwig, on precipitating the uric acid with silver nitrate, contains more nitrogen than corresponds to the uric acid obtainable from the specimen of urine. W. Cameron has utilised this behaviour for an approximate determination of the xanthin-substances. A process indicated by E. Salkowski can be applied for the same purpose.

The silver precipitate obtained (Salkowski-Ludwig) from 500 or 1000 c.c. of urine, after being carefully washed, is decomposed with hydrogen sulphide, and the filtrate is evaporated to dryness and extracted with sulphuric acid at 2 or 3 per cent. The uric acid then remains almost entirely undissolved; it is filtered off, washed, and weighed. The filtrate is rendered alkaline with ammonia, and again precipitated with a solution of silver. The precipitate obtained contains the so-called xanthine-substances along with minimum quantities of uric acid. Salkowski estimates its quantity at 8 to 10 per cent of the weight of the uric acid.

M. Krüger and C. Wolff (*Zeit. Physiol. Chemie*) have obtained in their experiments decidedly higher values (as a mean 0.26 per cent of the weight of the uric acid). Their process is founded on the precipitability of uric acid and of the xanthin-bases (Kossel and Krüger name them alloxur-bases) by copper sulphate and bisulphite. 100 c.c. of urine, free from albumen, are mixed when boiling with 10 per cent of a solution of sodium bisulphite, containing, in 100 c.c., 50 grms. of the salt, and immediately afterwards with 10 c.c. of a 13 per cent solution of copper sulphate, and then again heated to ebullition; 5 c.c. of a 10 per cent solution of barium sulphate are then added to promote settlement. After standing for two hours the precipitate is brought on a filter of Swedish paper, completely washed with water which has been previously boiled and cooled down to 50°, and then used, along with the filter, for determining the nitrogen by the Kjeldahl process. The value obtained gives the nitrogen of the uric acid plus that of the xanthin-bases. A simultaneous determination of the uric acid by the Salkowski-Ludwig process permits a calculation of the nitrogen belonging to the uric acid. The nitrogen of the xanthin-bases is found from the difference.

A process for determining uric acid, given by Denigès, differs from that of Haycraft only in the manner of titrating the silver. The author uses a process depending on the formation of potassium silver cyanide in an ammoniacal solution, using potassium iodide as indicator.—*Zeitschrift für Analytische Chemie*, xxxiii., p. 767.

Atomic Weights of Nickel and Cobalt.—Clemens Winkler.—The author has undertaken this re-determination in consequence of the published results of G. Krüger and F. W. Schmidt, and of H. Remmler. These results indicate that nickel and cobalt, as known at present, contaminated with an unknown element, so that the nickel and cobalt are not known in a pure state, and the atomic weights are not determined. Winkler gives atomic weight of nickel as 58.90, and that of cobalt 59.67.—*Zeitschrift für Analytische Chemie*, vol. xxxiii. Part 5.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JUNE 30TH, 1895.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, July 12th, 1895.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 166 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from June 1st to June 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 166 samples examined one was recorded as "slightly turbid," the remainder being clear, bright, and well filtered.

June has been a very dry month. Three-hundredths of an inch of rain fell at Oxford on the 1st, and eight-hundredths on the 11th. With these trifling exceptions no rain fell till the 26th, when there was a downpour of three-quarters of an inch. On the 28th nearly a quarter of an inch fell, followed on the 29th by two-hundredths additional, making a total of 1.12 inch. The mean of 25 years being 2.21, the deficiency is 1.09 inch. Unfortunately neither the river nor the country is much the better for the 1.12 inches falling in June. The bulk of this coming down on two stormy days near together, little time was allowed for the water to sink into the ground. The consequences being, swollen water courses for a few hours, a sudden flood in the river followed by as rapid a subsidence, and little if any permanent good, as compared with what would have been occasioned by the same amount of rain distributed over a greater number of days.

The purity of the Thames-derived waters is now at a very high level, and there is not much room for improvement in chemical quality; but that it is kept up and somewhat improved in all respects, the following table, giving the comparison between the composition of the waters in May and June of this year, is a satisfactory proof.

1895.—Averages of the Five Supplies derived from the River Thames.

Common Salt.	Nitric Acid.	Hardness.	Oxygen reqd.	Organic Carbon.	Organic Carbon.	Colour.
Per gall.	Per gall.	Degrees.	Per gall.	Per gall.	Per gall.	Br'n: Blue.
Means.	Means.	Means.	Means.	Maxima.	Means.	
May 1.994	0.908	14.41	0.045	0.128	0.206	13.5:20
June 1.951	0.903	13.85	0.034	0.081	0.100	11.4:20

Comparing the composition of the waters in June with that of the corresponding month last year shows an almost equally satisfactory result.

Bacteriological examinations of the waters from the general wells of the Water Companies, and from the unfiltered water of the river, have been proceeded with throughout the month. At the works the average number of microbes was 19, and in the river the average was 7625 microbes per c.c. The amount of impurity commu-

nicated to the river by a heavy storm following a long drought is shown by bacteriological examinations before and after the heavy storm on the 26th. Before the storm the Thames contained 3230 microbes per c.c., and immediately after the numbers rose to 29,032. This large increase produced no perceptible augmentation of the number of bacteria in the clear water wells of the respective Companies. A careful bacteriological examination of the water at the Companies' works on the days succeeding the storm showed that the filtration was effective, no appreciable increase being detected in the number of microbes present.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

A REVISION OF THE ATOMIC WEIGHT OF STRONTIUM.

FIRST PAPER: THE ANALYSIS OF STRONTIC BROMIDE.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 31).

Method of Analysis.

As in the case of baric bromide (*Proc. Amer. Acad.*, xxviii., 23), the silver required to precipitate all the bromine in strontic bromide was determined, as well as the amount of argentic bromide formed by the precipitation.

The chief problem which presented itself was the preparation of pure dry neutral bromide of strontium for weighing. In preliminary analysis the salt was ignited or fused in a platinum crucible, and weighed as the baric bromide had been. The decomposition of the salt was so great, however, that the uncertainty of the alkalimetric correction sometimes amounted to two or three tenths of a m.grm.; hence this method was clearly inadmissible.

The fusion of the salt in a platinum boat in a stream of nitrogen gave much better results, and two or three further preliminary determinations by this method gave promise of much greater accuracy. It is probable that the slight decomposition which occurred even in the atmosphere of nitrogen was due to the presence at 250–300° of a slight trace of moisture.

The presence of an excess of hydrobromic acid must necessarily lessen or prevent this decomposition; hence in three succeeding determinations (Nos. 13, 14, 15, below) pure dry hydrogen bromide was added to the nitrogen in which the combustion was conducted.

In these cases, however, the platinum boat, which had previously remained quite constant in weight, was evidently attacked, since upon one occasion (Exp. 15) it lost over two-tenths of a m.grm., and the pure white strontic bromide became tinged with a brown colour. The weight of the boat after each fusion was taken as the true weight, because the bromide of platinum, if formed, must precipitate nearly as much silver as the bromide of strontium.

In order to avoid the corrosion of the boat, hydrogen was added in small quantities to the mixture of gases. This, by preventing the dissociation of the hydrobromic acid, effectually preserved the platinum, and the boat remained constant in weight. The pure translucent or transparent colourlessness of the fused salt left nothing to be desired. A somewhat complex piece of apparatus was needed for the purpose. (See Fig. 1). A mixture of six volumes of pure nitrogen (made by passing air and ammonia over red-hot copper) and one volume of pure hydrogen was delivered from a gas holder through a succession of tubes of red-hot copper, dilute chromic and sulphuric

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy*.

acids, concentrated alkaline pyrogallol, and fused potash, into the arrangement for preparing hydrobromic acid. This, as well as all the apparatus following, was without rubber connections, the ground joints being made tight by means of syrupy phosphoric acid (Mo ley) and flexible by means of fine glass gridirons (Finkener). The pure dry nitrogen and hydrogen were led in the first place into a flask containing bromine, and then over asbestos and red phosphorus saturated with pure fuming hydrobromic acid. The bromine and hydrobromic acid were proved to be pure by the usual quantitative analysis, and the red phosphorus was ground and washed many times with pure water to free it as much as possible from chlorine (Stas). The mixture of pure slightly moist hydrogen bromide, nitrogen, and hydrogen was now dried by calcic bromide free from chlorine and iodine, and thus became ready for use.

The hard glass tube used for heating the platinum boat containing the strontic bromide was ground very tightly into its socket of soft glass, since it was not advisable to risk the presence of phosphoric acid here. The powdered nearly anhydrous strontic bromide, having been packed tightly into the boat and carefully pushed into position in the fusion tube, was thoroughly dried at 200° in a stream of pure air. The elaborate apparatus for preparing the mixture of gases was now connected with the fusion tube, and when all the air had been expelled the boat was slowly heated to cherry-redness until the strontic bromide was wholly fused. The temperature was then allowed to fall a little below 600° , and the solidified bromide of strontium was freed from any possible excess of hydrobromic acid by a current of dry hydrogen and nitrogen free from acid, delivered through a short-cut tube (see Fig. 1).

The almost red-hot boat was now transferred as quickly as possible to the light weighing bottle, within which it was allowed to cool. In the preliminary work (and in Analyses 13 and 14) this bottle was stoppered at once and cooled in an ordinary desiccator. Subsequently an improved desiccator was devised for this purpose. A wide glass tube capable of containing the weighing-bottle was drawn out at one end to a fine tube, which was fitted with a ground glass stopper. The other open end was made slightly conical and ground into a receptacle which was in its turn attached to a drying tube containing fused potash. The accompanying sketch supplements this description (Fig. 2).

While the boat was still hot within the fusion tube, the stopper of the weighing bottle was placed in the horizontal desiccator tube. The moment after the transference of the boat into the bottle, both together were slid into the momentarily opened desiccator tube by means of a glass rod which projected from the receptacle. The bottle was held by means of a glass carriage during this manipulation.

The open weighing bottle, with its stopper and fused contents, could now be heated indefinitely in a current of pure dry air at any temperature below the softening-point of soft glass. At the moment when it was desired to close the bottle, it was only necessary to elevate the desiccator tube from the horizontal to the vertical position, and the hot stopper fell automatically into the

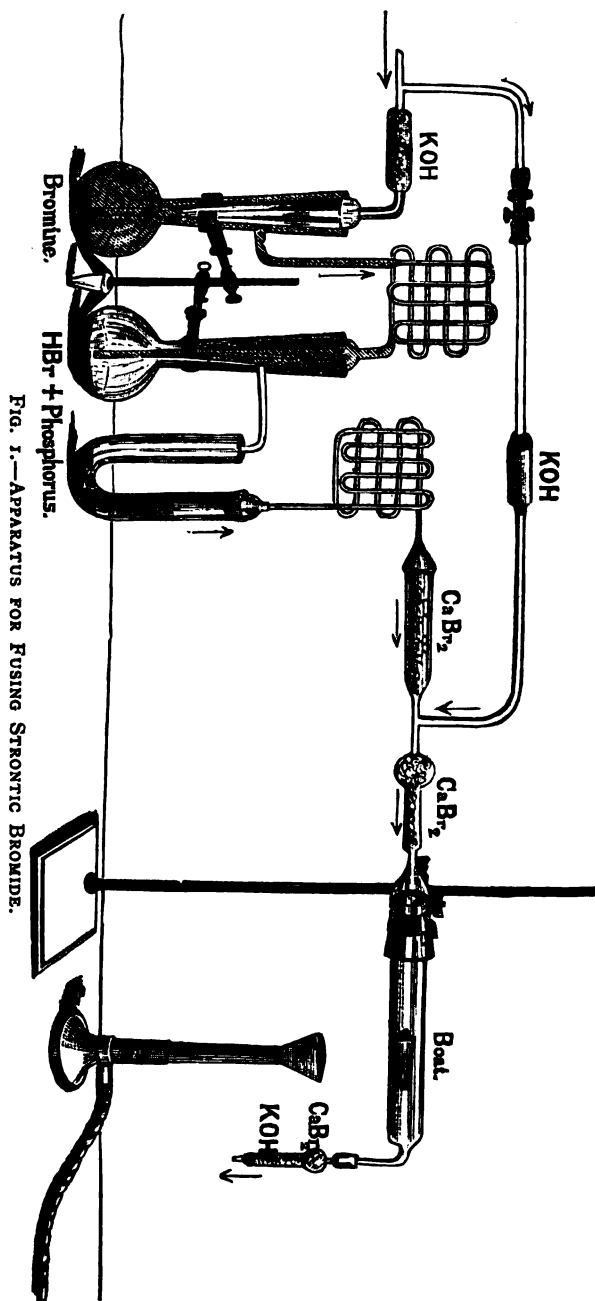


FIG. 1.—APPARATUS FOR FUSING STRONTIC BROMIDE.



FIG. 2.

equally hot bottle. The desiccator tube was now closed above, and allowed to cool at least four hours in the balance room. It is needless to say that before taking the final weighing of the bottle its stopper was loosened.

Having thus obtained as nearly as possible the true weight of the typical salt of strontium, the remainder of the analysis was conducted in a manner essentially simi-

lar to that adopted in the case of baric bromide (*Proc. Amer. Acad.*, xxviii., 24). Since it is unnecessary to describe again most of the precautions, nothing will be noted below excepting those particulars in which the details of the work differed from those already given. Two analyses, which were vitiated by known errors, are omitted from the tables.

(Pure dry nitrogen and hydrogen enter the apparatus through the tube at the left. The arrangement for preparing this mixture is not shown. Upon closing the pinchcock in the upper left-hand corner, the gases are driven through the flasks and charged with dry hydrobromic acid; upon opening the pinchcock, the hydrostatic pressure below causes the gases to flow through the upper short-cut tube and effectually sweep out the acid from the fusion tube. This latter tube, containing the boat in which the stromic bromide is fused, is at the right of the figure).

(To be continued).

ON CERTAIN PHENOMENA OBSERVED IN THE PRECIPITATION OF ANTIMONY FROM SOLUTIONS OF POTASSIUM ANTIMONYL TARTRATE.*

By J. H. LONG.

(Continued from p. 34).

In the above nothing has been said about certain peculiarities observed in the formation of the precipitates. When cold dilute solutions of borax and the tartrate are mixed no reaction takes place immediately, but with warm strong solutions, a precipitate seems to form as soon as the two liquids are poured together. In a former paper (*Journ. Anal. Appl. Chem., loc. cit.*) I pointed out the important and exceedingly curious fact that in the reaction between carbonates or acetates on the one hand, with the tartrate on the other, while no precipitate may appear immediately, perhaps not in hours, indicating a decomposition, the polarimeter shows that such has taken place. Here, also, we have evidence that a reaction has taken place even without precipitation, and this the polarimeter furnishes. The matter can be best explained by giving the details of several experiments.

I made five solutions by dissolving 5 grms. of the tartrate as before in 55 to 60 c.c. of warm water, cooled to 20°, and added certain weights of borax in small volumes of water, making the solutions finally to 100 c.c. at 20°. These solutions were polarised immediately in the 200 m.m. tube, with the following results:—

No. of expt.	$\text{K}_2\text{SbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ taken.	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ added.	α_D .
1	 5 grms.	0.5 grm.	12.08°
2	 5 "	1.0 "	9.40°
3	 5 "	2.0 grms.	5.53°
4	 5 "	3.0 "	4.10°
5	 5 "	4.0 "	3.75°

The normal rotation of the tartrate at 20° in the 200 m.m. tube, with a concentration of 5 grms. in 100 c.c., I have shown to be—

$$\alpha_D = 14.103^\circ.$$

The effect of the borax is therefore marked, but the extent of the decrease in rotation depends on the number of minutes intervening between the mixing of the solutions and the completion of the observation in the polarimeter. A gradual decrease in the readings was in all cases observed, until the solutions became finally too turbid for observation from the beginning precipitation. The first solution, for instance, in the above table was read as follows:—

10 hours, 30 minutes,	$\alpha_D = 12.08^\circ$
10 " 45 " "	" = 11.87°
10 " 55 " "	" = 11.80°

After standing some hours, the solutions deposited a precipitate and cleared up. On again polarising I found:—

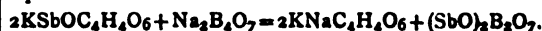
No.	α_D .
1	 11.52°
2	 9.01°
3	 5.29°
4	 3.92°
5	 3.65°

These observations were made in a 200 m.m. tube, but similar solutions were polarised in a 400 m.m. tube with perfect sharpness, the readings agreeing within 0.02°, as is possible with the large and excellent instrument used. I mention this to prove the perfect transparency of the liquids, and to show that the decreased rotations observed at the start were not due to any loss through precipitation, but were in consequence of changes preceding precipitation, these changes taking place very gradually.

We have here a phenomenon reminding one of the bi-rotation of solutions of certain sugars, but depending on a different cause undoubtedly. In the reaction between the same tartrate and sodium carbonate the same change was observed, but through a longer period. A solution containing in 100 c.c. one-tenth grm. of the carbonate and 5 grms. of the tartrate gave, at the end of five minutes in a 400 m.m. tube, a rotation of 25.582°, after thirty minutes, 25.580°; that is, practically the same; but after twelve hours, 24.480°. A perfectly clear mixture can be made containing 5 grms. of the tartrate and nine-tenths grm. of sodium carbonate in 100 c.c. When polarised immediately, I found with this in the 400 m.m. tube $\alpha_D = 11.57^\circ$; after ten minutes, 11.50°; after twenty-five minutes, 11.132°; and after sixty-five minutes, 10.55°.

In the normal reaction between carbonates or borates and the potassium antimonyl tartrate a precipitate should be formed, but we find that at a low temperature this is much delayed. If precipitation alone were taken as the indication of a reaction it would necessarily appear that at the outset no reaction takes place, but the behaviour with polarised light shows the error in this view. It is evident that a reaction begins immediately and progresses far toward completion in some of the cases considered before even the first polarisation can be made; that is, within two or three minutes. This first part of the reaction is the beginning stage of precipitation and may consist in the formation of some intermediate product, which finally decomposes. I have elsewhere shown (*Am. Journ. Sci. and Arts, loc. cit.*) that the rotation of potassium sodium tartrate is decreased by the addition of sodium, thallium, and lithium salts, but is increased by the addition of potassium and ammonium salts, and that this reaction is fully accounted for if we assume the formation of sodium tartrate, sodium-thallium tartrate, or sodium-lithium tartrate in the one case, or of potassium or potassium-ammonium tartrate in the other. In the present instance we evidently must admit the formation of sodium-potassium tartrate from the instant the solutions are mixed, but that the reaction is a progressive one. The potassium antimonyl compound with a high rotation gives place to the potassium-sodium compound with a much lower rotation. There is nothing to show, however, in what form the antimony is held.

Possibly the reaction may be explained by assuming the formation of an intermediate product according to this equation:—



If the last compound is formed it must break up in this manner—



leaving a hydrated oxide of antimony with more water than the final precipitate contains. By loss of water, possibly, this hydrated compound must, in time, settle out as a precipitate. It has been explained that, by boiling, the precipitate forms and subsides soon. At 20°, even after what I have called the preliminary stage of precipitation, may have occupied hours, the actual formation of the precipitate may consume an equally long time. The

* *Journal of the American Chemical Society*, vol. xvii, No. 2.

precipitate is a growth through an invisible and a visible stage, and what is true here is true of the next case to be given.

Reaction with Sodium Tungstate.

Cold solutions of the tartrate give no immediate precipitate when mixed with cold solutions of ordinary sodium tungstate, but on standing the mixtures gradually become turbid, and finally deposit a sediment. The composition of this depends largely on the temperature and concentration. The precipitate formed in the cold, collected, and dried at 105–110° C., consists essentially of antimony oxide. A precipitate formed by mixing hot solutions has practically the same composition, but if obtained after long heating it contains a relatively larger amount of tungstic acid.

In a series of tests made by mixing hot solutions of the two salts, and allowing the mixtures to stand several hours to cool, the following results were obtained:—

KSbOC ₄ H ₄ O ₆ ·1½H ₂ O in 100 c.c.	Na ₂ WO ₄ ·2H ₂ O in 50 c.c.	Weight of precipitate.	Sb ₂ S ₃ from same precipitate.	Percent Sb in precipitate.
1 grm.	2 grms.	0.3087	0.3467	80.22
2 grms.	2 "	0.6442	0.7291	80.84
4 "	2 "	0.5728	0.6486	80.88
5 "	2 "	0.7222	0.8170	80.79

The mixtures were made in platinum dishes holding about 200 c.c., and as the precipitates formed as a coherent coating on the dishes they were easily washed, dried at 110°, and weighed. They were then dissolved in diluted hydrochloric acid, which left a small amount of tungstic acid in each case in flocculent form. The solutions were then filtered, and, after the addition of some tartaric acid, were precipitated by hydrogen sulphide in the usual manner. The sulphide precipitates were collected on a Gooch, dried at 110°, and weighed. It will be seen that the results are a little low to correspond to pure antimony oxide as the composition of the white precipitate. This compound contains 83.3 per cent of antimony. The compound Sb₂O₃·H₂O contains 78.4 per cent. The lower results are doubtless due to the small amounts of tungstic acid left in each case on treatment with hydrochloric acid, and referred to above.

In a second series of experiments constant amounts of the tartrate in hot solutions were mixed with varying amounts of the tungstate, likewise in hot solution. The white precipitates which formed were collected and weighed as before, with the following results, which show the effect of excess of tungstate on the amount of precipitate. In each case 2 grms. of the tartrate were taken in 100 c.c., and the tungstate in 50 c.c.

Tungstate taken.	Precipitate obtained.
0.5 grm.	0.1070
1.0 "	0.4598
2.0 grms.	0.5762
3.0 "	0.5861
4.0 "	0.6143
5.0 "	0.6185

From this, it is plain that the amount of precipitate is not much increased by great excess of the tungstate beyond a certain point. In the cold, precipitation is much less perfect, while, by boiling, fully three-fourths of the theoretical yield of oxide from the tartrate can be obtained.

By working with cold solutions a mixture may be made which remains clear long enough to permit polarimeter observations to be taken. I dissolved 5 grms. of the tartrate in 60 c.c. of water, cooled to 20°, and added five-tenths grm. of the tungstate in 20 c.c. of water. The mixture was made up quickly to 100 c.c. at 20° and polarised in the 200 m.m. tube immediately and after intervals of five minutes. I found without re-filling the tube:—

First observation	$\alpha_D = 11.66^\circ$
Second "	12.03°
Third "	12.13°
Fourth "	12.53°

The solution became now too turbid, from separation of a precipitate, for further tests. On standing some hours, the remainder of the solution in the flask cleared after subsidence of its precipitate. A portion of this examined gave—

$$\alpha_D = 12.74^\circ.$$

Another portion of the same solution, heated and then cooled to 20°, gave the same. A new solution prepared in the same manner gave, after standing some time,—

$$\alpha_D = 13.11^\circ.$$

I made next a solution containing in 100 c.c. 5 grms. of the tartrate and 1 grm. of the tungstate. This examined, immediately, at 20°, gave—

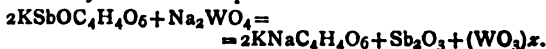
$$\alpha_D = 9.42^\circ,$$

but it soon became turbid and deposited a precipitate. After clearing, I found—

$$\alpha_D = 11.48^\circ,$$

which increased to 11.87° by heating the liquid.

These reactions are especially interesting when compared with those between the tartrates and other salts. We have here, as before, a marked decrease in the specific rotation on mixing the solutions of the active and inactive substances. But in the case of the tungstate, on standing, there is an increase instead of a decrease in the rotation observed in the other cases. This behaviour finds its explanation probably in the action of the liberated tungstic acid. The reaction between the two salts undoubtedly follows this equation:—



The precipitation of the tungstic acid is very slow and incomplete. While in solution, it may combine with the soluble tartrate to form a body with increased rotation, the possibility of which is shown by the researches of Gernez and others. The delay in the appearance of the precipitate may be due to the formation and slow breaking up of intermediate products containing the antimony and tungstic oxides in temporarily soluble condition. With liberation of the tungstic acid we have a gradual increase in the already decreased rotation. This change in the rotation, before precipitation, is well shown in the following observations. I dissolved 5 grms. of the tartrate and 2 and five-tenths grms. of the tungstate, mixed at a low temperature and made up to 100 c.c. as before, and at exactly 20° C. A reading with the 200 m.m. tube was made as soon as possible, and, without changing the solution, this was repeated at frequent intervals. The results were as follows:—

3 hours 28 minutes	$\alpha_D = 5.66^\circ$
"	" = 5.96°
"	" = 6.45°
"	" = 6.83°
"	" = 7.15°
"	" = 7.32°
3 hours 44 minutes	" = 7.43°
3 hours 58 minutes	" = 7.90°

At this point the liquid began to grow slightly turbid, so that the observations could not be continued. The remainder of the liquid was then heated in a closed flask to complete the precipitation, cooled to 20°, and tested. I found now—

$$\alpha_D = 9.13^\circ.$$

The liquid still remaining was filtered, 50 c.c. of the filtrate taken and precipitated with hydrogen sulphide, yielding finally 0.4045 grm. of antimony sulphide. From this it appears that, of the tartrate originally taken, 1.599

conform to the "law of definite relation" of opticity and reducing power.

From this we have—

KSbOC₄H₄O₆.½H₂O decomposed = 3.401 grms.

$\text{KNaC}_4\text{H}_4\text{O}_{6.4}\text{H}_2\text{O}$	remaining formed	1.599 2.888	" "
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Now, the rotation corresponding to the tartar emetic remaining is $4^{\circ}50'$, and that to the Rochelle salt formed is $1^{\circ}25'$, from which we should expect a total rotation of $5^{\circ}75'$. This, in fact, corresponds very nearly to what was observed at the beginning of the test, and seems to bear out the suggestion made above: viz., that the principal reaction here occurs before actual precipitation appears. A splitting of the tartar emetic is indicated by the immediate decrease in the rotation, and then the complex effect of addition of the liberated tungstic acid to the alkali tartrate in solution appears from the gradually increased rotation. Precipitation finally follows as the end of the reaction; the separated part assumes the insoluble form.

It will be recognized that the phenomenon in this case is much more complex than in the other. There is nothing to show that while the rotation is being increased by the action of the tungstic acid there is not also a tendency toward decrease because of progressive decomposition of the potassium antimonyl tartrate. In all probability the observed rotation is a resultant effect.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 20th, 1895.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

Extraordinary General Meeting.—The following change in the Bye-laws was proposed from the Chair, and passed.

In Bye-law 1, the last paragraph, beginning "The life composition fee," was struck out and the following inserted:—

"The life composition fee shall be Thirty Pounds, excepting that Fellows who have paid ten annual subscriptions shall pay as life composition fee Twenty Pounds; Fellows who have paid fifteen annual subscriptions shall pay Fifteen Pounds; Fellows who have paid twenty annual subscriptions shall pay Twelve Pounds; and Fellows who have paid twenty-five annual subscriptions shall pay Ten Pounds."

At the ordinary Scientific Meeting which followed, Messrs. George J. Ward, John Wilson, E. S. Barralet, and W. A. Greaves, were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Edward Henry Farr, Uckfield; Edward Henry Grossman, 12, Alfred Place West, S.W.; C. E. Harrison, 53, Lansdowne Road, W.

The following were duly elected Fellows of the Society:—John Croysdale, Joseph Lones, James Morison, Arthur E. Potter, M.A. B.Sc., Edwin James Read, B.A., Albert Joseph Simons.

Of the following papers those marked * were read :—

"81. "On the 'Isomaltose' of C. J. Lintner." By HORACE T. BROWN, F.R.S., and G. HARRIS MORRIS, Ph.D.

The paper gives a detailed account of the authors' investigations into the nature of Lintner's "isomaltose," and their results are summed up in the following conclusions:—

IX. When the products of a starch-transformation by diastase are submitted to any known process of fractionation, the properties of each and every fraction strictly

2. The "isomaltose" of C. J. Lintner is not a chemical entity, but can be further split up by careful fractionation with alcohol and by fermentation, in such a manner as to indicate that it is a mixture of *malto*se and dextrinous substances of the malto-dextrin or amyloïn class. We must therefore cease to use this term "isomaltose" in relation to any of the products of the diastatic conversion of starch.

3. The crystallisable osazone which Lintner has described as "isomaltosazone," and upon which he has mainly founded his belief in the existence of "isomaltose," is nothing but "maltosazone" modified in its crystalline habit and melting-point by the presence of small but variable quantities of another substance.

4. The substance or substances which are capable of thus modifying maltosazone are the products of the action of phenylhydrazine on the dextrinous substances mentioned in 2.

5. This can be shown (1) *analytically*, by careful fractionation of the starch-products by alcohol, and also by fermentation; and (2) *synthetically*, by the re-crystallisation of pure maltosazone in the presence of the non-crystallisable products of the action of phenylhydrazine on the maltodextrins.

6. The only substance amongst the products of starch-transformation by diastase which is capable of yielding a crystallisable osazone, is *maltose*.

7. The results of the investigation bring out very clearly the danger of attempting to identify the carbohydrates in mixtures solely by the properties of their osazones, as these properties are liable to considerable modification by other substances of the same class which may not in themselves be crystallisable or readily separable from aqueous solutions.

DISCUSSION.

Mr. ARTHUR R. LING claimed priority on behalf of himself and Mr. J. L. Baker in having pointed out that Lintner's so-called isomaltose is not a homogeneous compound (*Proc. Chem. Soc.*, 1895, 3). In this communication they had also adduced strong evidence in favour of the view that the so-called isomaltose is a mixture of maltose and the simple dextrin, $C_{12}H_{20}O_{10}$, and they had proved that the osazone melting at $150-152^\circ$ has the composition of a hexatriosazone.

82. "*Action of Diastase on Starch: Nature of Lintner's Isomaltose.*" By ARTHUR R. LING and JULIAN L. BAKER.

In a previous communication (*Proc. Chem. Soc.*, 1895, No. 146, 3) the authors have described the isolation of a substance from the transformation-products of starch by the diastase prepared from low-dried or green malt. This substance had approximately the optical and cupric reducing powers of Lintner's so-called isomaltose. Analyses and cryoscopic determinations made with this substance indicated that it had the molecular formula $C_{12}H_{22}O_{11}$; but the essential difference between it and the so-called isomaltose of Lintner was that it yielded maltosazone together with a very small quantity of an osazone melting at $145-152^{\circ}$ on treatment with phenylhydrazine acetate, whereas Lintner states that his compound yields a single characteristic osazone melting at $150-152^{\circ}$. The authors have examined the low melting osazone obtained from their product, and conclude that it is merely impure maltosazone. More recent experiments carried out by the authors support their view that Lintner's so-called isomaltose consists of a mixture of maltose and the simple dextrin, $C_{12}H_{20}O_{10}$ (*loc. cit.*). No glucose is present among the products of the action of diastase from low-dried malt on starch, and diastase from this source is without action on maltose.

It was previously shown (*loc. cit.*) that when starch is transformed at 70° with the diastase prepared from kiln-dried or brewer's malt, the fraction which should correspond with Lintner's isomaltose gives, on treatment with

phenylhydrazine acetate, glucosazone together with an osazone agreeing in crystalline appearance and melting-point with the so-called isomaltoosazone of Lintner, but having the composition $C_{18}H_{30}O_{14}(N_2HPh)_2$, as if derived from a *hexatriose*, $C_{18}H_{32}O_{16}$. A diligent search has therefore been made for this triose among the transformation products last mentioned, but no crystalline compound has been isolated from them with the exception of maltose. Glucose was invariably present in small amount, and the authors find that when maltose is treated at 70° for two hours with the diastase prepared from high-dried malt, the presence of about 20 per cent of glucose is indicated by the increased cupric reducing power and the diminished optical activity; glucose was also detected qualitatively by the production of glucosazone. Bearing in mind the presence of glucose, as also their suggestion that Lintner's isomaltoosazone contains the simple dextrin, it occurred to the authors that the triosazone was possibly produced by the interaction of this dextrin and glucose with phenylhydrazine; and this turns out to be the case. When the supposed isomaltoosazone is treated with phenylhydrazine acetate in presence of glucose, the portion of the product soluble in hot water consists of a mixture of the triosazone and maltosazone.

*83. "The Transformation of Ammonium Cyanate into Urea." By JAMES WALKER, D.Sc., Ph.D., and F. J. HAMBLEY.

The transformation of ammonium cyanate into urea is reversible, about 5 per cent of urea in decinormal aqueous solution at 100° being re-transformed into ammonium cyanate. The direct transformation obeys the laws of a bimolecular reaction, and not of a unimolecular reaction, as might be expected. This is accounted for by the assumption that the ammonium cyanate is largely dissociated into ammonium ions and cyanic ions, and this assumption is confirmed by the influence of ammonium sulphate, potassium sulphate, potassium cyanate, and other substances, on the rate of the reaction. The dissociation theory also enables us to calculate the quantitative phenomena taking place when the transformation of urea into ammonium cyanate occurs in presence of silver nitrate. The speed of the reaction varies greatly with the temperature, and the variation may be expressed by means of van't Hoff's formula.

*84. "Note on the Transformation of Ammonium Cyanate into Urea." By H. J. H. FENTON, M.A.

Some years ago the author made a short communication to the Cambridge Philosophical Society upon this subject. ("The Metamerism Transformation of Ammonium Cyanate," *Proc. Camb. Phil. Soc.*, 1888, 307.) Details of these experiments were not published, as it was intended to make further experiments. The reason for giving these details in the present note is that, in the list of papers to be read at the present meeting, there is one which has the above title, and it was thought that the observations might be of interest to the authors. Unfortunately the *Proceedings of the Cambridge Philosophical Society* are not often seen by chemists outside Cambridge, so that it is hardly to be expected that these authors should be aware of this communication.

In a previous paper (*Trans. Chem. Soc.*, 1878) I showed that urea when treated with sodium hypochlorite, in presence of caustic soda in the cold, evolves only one-half of its nitrogen in the free state, the remainder being retained in form of cyanate. The latter gives no nitrogen with hypochlorite or hypobromite.

Ammonium cyanate was prepared by direct union of cyanic acid vapour and dry ammonia. Weighed portions of this salt were acted upon by sodium hypobromite and hypochlorite, and excess of soda, with the following results:—

With sodium hypobromite—

- I. 0.0544 grm. AmCyO gave 9.3 c.c. nitrogen (corr.).
II. 0.0562 " " " 9.93 " "

Since with hypobromite estimations, as conducted in the usual way, there is a deficiency of about 8 per cent in the nitrogen evolved, a correction for this was applied, giving (I.) 10.10 c.c., and (II.) 10.79 c.c. Theory for half the nitrogen requires 10.11 c.c. and 10.45 c.c. respectively.

With sodium hypochlorite—

				Theory for $\frac{1}{2} N_2$
0.0620 grm. AmCyO	gave	11.89 c.c. nitrogen (corr.)	11.53	
0.0692 " "	"	" 13.08 " "	12.87	
0.0905 " "	"	" 16.34 " "	16.83	

It is evident, therefore, that this salt evolves only half its nitrogen in the free state with either reagent.

These facts obviously suggest a method by which it is possible to estimate the extent to which ammonium cyanate has been transformed into urea.

Let V = volume of nitrogen obtained by the action of hypobromite when a given weight of ammonium cyanate is taken and partly or entirely converted into urea; and let V_1 = total volume of nitrogen contained in the substance taken. Then the nitrogen due to the urea formed will be $2V - V_1$. For convenience the percentage transformation may be expressed as $2V - V_1/V_1 \times 100$.

Applying this method, the following results were obtained:—

0.7632 grm. AmCyO was dissolved in water and the solution made up to 100 c.c. 10 c.c. were taken for each experiment.

	Temp.	Time.	Vol. of N_2 (corr.)	Theory for $\frac{1}{2} N_2$	Transformation.
I. Ordinary		Immediate	14.14	14.19	None
(about 19°)					
II. 37°		18 hours	19.0	—	33.8
III. 37°		3 days	20.54	—	44.7

0.5561 grm. AmCyO dissolved in water and made up to 100 c.c. 10 c.c. taken.

I. Ordinary	20 hours	12.60	10.34	20.3
II. —	—	12.28	—	—
III. 100°	1 hour	17.57	—	69.9
IV. 100°	2½ hours	19.03	—	84.0
V. 100°	20 hours	19.50	—	88.5

0.9495 AmCyO in 100 c.c. 10 c.c. taken.

I. 70°	1 hour	25.9	17.66	46.6
II. 70°	4 hours	28.5	—	61.3
III. 70°	40 hours	30.4	—	72.1

In each case the liquid was measured into a small, partly drawn off test-tube, which was afterwards sealed. A correction for the loss of 8 per cent is made in the stated volumes of nitrogen.

These results indicate that the change proceeds rapidly at first, then becomes slower, and finally reaches a limit which is a function of the temperature. In no case examined was the transformation complete.

These facts suggest that the action may be a reversible one; urea and ammonium cyanate are perhaps tautomeric forms transformable one into the other. This hypothesis would account for some of the properties of urea which are otherwise difficult to understand. For example, the difference in the actions of hypobromite and hypochlorite (in presence of soda), mentioned above, might be explained in the following way:—The action of hypobromite is nearly instantaneous, whereas that of hypochlorite is extremely slow. The solution of urea may contain urea and ammonium cyanate in a state of equilibrium, the urea, of course, largely preponderating. Hypobromite therefore evolves nearly all the nitrogen—all from the urea, and half from the ammonium cyanate. Hypochlorite, however, it may be supposed, attacks only the ammonium cyanate, liberating half of its nitrogen, the other half remaining as cyanate which is not further decomposed. This would destroy the equilibrium of the system, and the further transformation of urea into ammonium cyanate would result. The latter would be removed as before, and

finally one-half of the total nitrogen would be evolved in the free state,

There are indications also that cyanate is produced when urea solution, mixed with potash in excess, is left to stand for several weeks in a bell-jar over sulphuric acid. This fact could be explained in a similar manner.

*85. "Some Derivatives of Humulene." By ALFRED C. CHAPMAN.

In a former communication (*Trans. Chem. Soc.*, 1895, lxvii., 54) the author described a sesquiterpene obtained from the essential oil of hops by fractional distillation, for which he suggested the name humulene. In that paper a nitrosochloride (m.p. 164—165°) was described, and also a nitrol-piperide obtained from it (m.p. 153°).

In the present paper the author gives an account of the following additional humulene derivatives:—

Hydrochloride of humulene nitrol-piperide—
($C_{15}H_{24}NO \cdot NC_5H_{10} \cdot HCl$).

—This was obtained by passing dry hydrogen chloride into a solution of the nitrol-piperide in ether. The platinum-chloride of this salt crystallising from alcohol in reddish needles was also prepared (m.p. 187—189°).

Humulene nitrol-benzylamine—
($C_{15}H_{24}NO \cdot NHCH_2C_6H_5$).

—This compound was obtained by heating humulene nitrosochloride with an excess of benzylamine. After crystallisation from boiling alcohol it melted at 136°. The hydrochloride of this base was prepared by passing hydrogen chloride into an ethereal solution of the compound (m.p. 187—189°).

Humulene nitrosate ($C_{15}H_{22}N_2O_4$).—Prepared by acting with nitric acid upon a mixture of humulene and amyl-nitrite in glacial acetic acid. It crystallises from benzene in small colourless needles, melting at 162—163°.

Humulene nitrosite ($C_{15}H_{24}N_2O_3$).—This compound was prepared by allowing nitrous anhydride to combine with humulene dissolved in petroleum ether. After one re-crystallisation from boiling alcohol the compound was obtained in the form of magnificent deep blue needles, melting at about 120°. The mother-liquor from which this compound separated deposited colourless needles, which, after re-crystallisation, melted at 166—168°, and were found to be isomeric with the blue compound. This latter could be almost completely converted into the white substance by the long-continued boiling of its alcoholic solution.

*86. "Note on Thio-derivatives from Sulphanilic Acid." By L. EDNA WALTER.

When diazotised sulphanilic acid and potassium xanthate are allowed to interact, following Leuckart's directions (*J. Pr. Chem.*, 1890, xli., 179), the parasulphonate-xanthate of the formula $SO_3K \cdot C_6H_4 \cdot S \cdot CS \cdot OEt$ is readily formed as an easily soluble crystalline salt. On hydrolysis this xanthate undergoes change in two ways, and yields both the sulphhydryde, $SO_3K \cdot C_6H_4 \cdot SH$, and the sulphthide, $SO_3K \cdot C_6H_4 \cdot S \cdot Et$. As the former, however, is very readily oxidised, the corresponding disulphide is usually obtained. When acid is used in effecting hydrolysis, the disulphide is the only product; but when alkali is used the product is a mixture which apparently is the richer in sulphthide the more concentrated the alkali.

When the dried xanthate is heated at about 200° it loses considerably in weight, being converted into the sulphthide, which is more easily prepared in this way: only a small amount of disulphide is produced in this case.

The potassium disulphide crystallises in needles; it is very soluble in water, and sparingly soluble in alcohol. It yields a crystalline sulphochloride melting at 142°, and a sulphonamide melting at 253°.

The potassium sulphthide is very soluble in water and in alcohol; it crystallises in six-sided plates. The barium salt crystallises in very characteristic rhombic plates; its sulphochloride melts at 33°, and its sulphonamide at 134°.

The sulphthide is converted by oxidation with permanganate into the corresponding sulphonate, which is soluble in water, and yields a sulphochloride melting at 103·5°.

The sulphide, on the other hand, very readily yields benzeneparadisulphonate when oxidised by permanganate. The xanthate may also be directly converted into paradisulphonate by oxidation with permanganate, and it is easy in this manner to prepare any desired quantity of benzeneparadisulphonic acid.

One disulphochloride, $C_6H_4(SO_2Cl)_2$, prepared from the product, fuses at 136·5, several degrees higher than the melting-point assigned by Körner and Monselise.

*87. "Helium, a Constituent of Certain Minerals." Part II. By WILLIAM RAMSAY, F.R.S., J. NORMAN COLLIE, Ph.D., and MORRIS TRAVERS, B.Sc.

The first part of this communication contains an account of the sources of helium. About thirty minerals have been investigated, mainly those containing uranium, and of these fifteen contained helium in greater or less amount. Many, in addition, evolved hydrogen, a hydrocarbon, and carbon dioxide.

The second part treats of the densities of samples from different sources. After purification, the value 2·2 was obtained for three samples—one from cleveite, one from bröggerite heated alone, and one from bröggerite fused with hydrogen potassium sulphate. It was proved during these experiments that hydrogen is not evolved in combination with helium by the action of acid on mineral containing helium. The density of all these samples, united and carefully purified, was 2·218; a second purification made the density 2·228, practically an identical number.

The wave-length of sound in the gas corresponds accurately to the ratio 1 : 18, implying monatomicity, if that be granted to mercury on the same and on different grounds. The atomic weight would therefore be 4·4.

The solubility in water is 0·007 at 18°. Helium is therefore the least soluble of gases. It is insoluble in alcohol and in benzene.

The paper concludes with a discussion of the relations of helium towards other elements.

88. "New Formation of Glycollic Aldehyde." By H. J. H. FENTON, M.A.

The properties of the acid $C_4H_4O_6 \cdot 2H_2O$, which was described by the author in a previous paper (*Trans. Chem. Soc.*, 1894), are still being investigated with a view of establishing the constitutional formula for the acid. The present paper deals with the decomposition which the acid undergoes when heated with water. It is shown that, under these circumstances, glycollic aldehyde and carbon dioxide are produced, the change taking place almost quantitatively according to the equation—



The glycollic aldehyde was identified by oxidation to glycollic acid and by the action of excess of phenylhydrazine acetate, which gave the phenylosazone of glyoxal.—



This decomposition affords a very simple method for the preparation of glycollic aldehyde.

By spontaneous evaporation of the aqueous solution (and purification from a trace of glyoxylic acid produced) the aldehyde was obtained in an isolated condition as a viscid syrup, pure, except for a trace of ether or alcohol, which is obstinately retained. On removing this ether by heating under reduced pressure, the aldehyde undergoes polymerisation, a sweet-tasting solid gum being the result. Molecular weight determinations indicate that this substance is a form of hexose, $C_6H_{12}O_6$. It reduces Fehling's solution in the cold, and gives an osazone melting at 162—163°.

89. "Ethereal Salts of Ethanetetra-carboxylic Acid." By JAMES WALKER, Ph.D., D.Sc., and J. R. APPELYARD. Symmetrical dimethyl dihydrogen ethanetetra-carboxylate should, according to stereochemical theory, exist in an inactive and a racemic modification, and the corresponding potassium salts should yield, on electrolysis, dimethyl maleate and dimethyl fumarate respectively. An attempt was made to separate the two modifications, but it was unsuccessful. The mixed dimethyl dipotassium salts, on electrolysis, gave a small quantity of dimethyl fumarate. The following derivatives of ethanetetra-carboxylic acid were prepared in the investigation. Tetra-methyl salt, m. p. 104°, symmetrical. Dihydrogen dimethyl salt, m. p. 158–160° with decomposition. Triethyl monomethyl salt, m. p. 58°. Diethyl dimethyl salt, liquid.

90. "On the Occurrence of Argon in the Gases Enclosed in Rock Salt." By P. PHILLIPS BEDSON, M.A., D.Sc., and SAVILLE SHAW.

The brine obtained from the wells sunk in the rock salt deposit on the north bank of the Tees, in the neighbourhood of Middlesbrough, when pumped to the surface is found to be strongly effervescent. The gas, the liberation of which gives rise to this phenomenon, had been analysed by one of us some years ago (*J. Soc. Chem. Ind.*, 1888, 660 to 667), and found to consist of—

	By volume.
Methane	2'05
Nitrogen	97'95
	100'00

It was thought that a re-examination of this gas, with a view of testing its freedom or otherwise from argon, would be of interest. Through the kindness of Mr. Alfred Allhusen, a fresh sample was accordingly procured in May of the present year, when it was found to have slightly altered in composition and to contain—

	By volume.
Oxygen	1'3
Nitrogen	98'7
	100'0

only a minute quantity of methane being present, and the small amount of oxygen probably due to air leakage.

Professor Ramsay kindly furnished details of the simplest method for ascertaining the presence of argon in the gas—"sparking" over caustic soda in presence of oxygen, and submitting the residue after contraction ceased to spectroscopic examination. A small induction coil, giving a $\frac{1}{2}$ -in. spark in air and actuated by the current from a battery of storage cells, was employed. About 40 c.c. of the gas was submitted to examination in each experiment. The sparking was continued in presence of an excess of oxygen until no further contraction was noticeable. After this it was found necessary to continue the sparking for an hour or two, until examined spectroscopically the nitrogen lines, which grew fainter and fainter, finally disappeared. After absorbing the excess of oxygen present with alkaline pyrogallate, the small residue was added to an already measured volume of pure oxygen, and the whole accurately measured, using the apparatus of Professor Dittmar in conjunction with a form of Lunge volumeter.

Two estimations gave results as follows:—

I. 1'205	Mean = 1'24 per cent of argon.
II. 1'269	

The amount of argon present in the nitrogen from the rock salt is thus practically identical with the amount present in the nitrogen of ordinary air as determined by Lord Rayleigh and Professor Ramsay. This is to the authors' knowledge the first recorded analysis of a sample of naturally occurring nitrogen which has been stored up for some thousands of years under conditions which practically preclude the possibility of change. The nitrogen was probably in the first instance derived from the atmo-

sphere, and it is of considerable interest to note that atmospheric nitrogen at the present day is still associated with the same percentage of argon as when in remote ages it was first occluded in cavities in the rock salt.

As Professor Ramsay has shown that argon is soluble to a considerable extent in water, it is proposed to examine the gas given off on boiling the brine after effervescence has subsided. In this way a gas would probably be obtained much richer in argon, and, as there would be little difficulty in procuring it in quantity, it might prove a useful source of the new gas. It is also proposed to submit the nitrogen found enclosed in coal to a similar examination.

91. "On the Dissociation of Gold Chloride." By T. K. ROSE, D.Sc., A.R.S.M.

The tensions of dissociation of trichloride of gold at various temperatures up to 330° were measured, the limited chemical action investigated being expressed by the equation—



The total pressures observed when a mixture of AuCl_3 and AuCl is heated in a closed space are higher than the tensions of dissociation, owing to the vapour-pressure of AuCl_3 , which becomes considerable between 200° and 300°. The attainment of the maximum pressure is greatly delayed if the substances are carefully dried.

An investigation by means of Deville's "hot and cold tubes" showed that AuCl_3 undergoes continuous volatilisation in chlorine gas at atmospheric pressure at all temperatures between 180° and 1100°, the limits of temperature employed. The curve illustrating the rate of volatilisation under these conditions passes through a maximum at about 300°, and a minimum between 800° and 900°. Reasons for the shape of the curve are adduced.

The results afford evidence that Krüss's statements on the decomposition and volatilisation of gold chloride cannot be substantiated, but that those of Boyle and of Debray are in accordance with fact. It is pointed out that, according to the laws of chemical equilibrium, compounds formed with evolution of heat cannot be included in the class of bodies which are completely decomposed at moderate temperatures and again formed at much higher temperatures. The statements of Krüss regarding the behaviour of gold chloride at various temperatures, and those of Langer and V. Meyer regarding platinum chloride, are therefore at variance with theory, and in the former case have been shown to be unfounded.

(To be continued.)

NOTICES OF BOOKS.

Chemists and their Wonders. The Story of the Applications of Chemistry to various Arts and Manufactures. By F. M. HOLMES. London: S. W. Partridge and Co. Crown 8vo., pp. 160.

THE reader will find here a readable, bright, and most instructive survey of the services which chemistry is rendering to civilisation. It is drawn up in the form of a conversation between several interlocutors, one of whom, aptly spoken of as "Mr. Flippant," does not think much of chemistry until fairly beaten off the field. He pleads that "chemists don't build bridges or make railway trains!" We may here mention that there exists in the minds of County Councillors, &c., a delusion that chemists are inferior to engineers, and they even hand over to the latter work which can be done aright only by the former. Thus, when the manner of disposing of the sewage of London was under discussion, it was proposed that the task should be assigned to the engineer who had constructed the Tay Bridge!

Another school of unqualified censors accuse us of "imperfect drainage, of devising benumbing poisons, and

contriving infernal machines." Whilst a third, though kindred, faction think that we might be good and happy without any knowledge of rare earths, or even if they had no existence. Our author does much to sweep such cobwebs out of the heads of all sensible people.

In his sketch on the rise of alchemy, however, he concedes too much to the old notion that this romantic delusion was the parent of chemistry. This question has been of late exhaustively discussed by the great French *savant* Berthelot. A little further Mr. Holmes touches on the peculiarly English error that chemistry is especially connected with drugs and medicines. This mistake is due to the unfortunate fact that in these realms the dealers in, and compounders of, medicines have contrived to appropriate the term "chemists" in place of their legitimate name, "pharmacists."

In the work we find an exposition of the most salient features of the lives and researches of Boyle, of Lavoisier, Chevreul, of John Young (of "paraffin" celebrity), of John Walker, of Scheele, of W. Murdoch (the gas manufacturer), with his predecessors, Shirley and Clayton, the latter dating back to 1739. Winzer, or Winsor as he renamed himself, receives mention, and though he did not invent gas, was the inventor of gas companies—a blessing for which chemical science can scarcely be held responsible.

The expression here used of "enriching" coal-gas with both oil-gas and water-gas is misleading. Water-gas, sometimes spoken of as "Dowson gas," enriches coal-gas chiefly in the deadly product carbon monoxide. A speaker here doubts whether it would answer well in England if used alone. The reason is because our sanitary laws are more stringent than those of the United States.

"High" explosives receive a very full notice. As a set-off to the fearful dangers consequent upon any oversight or irregularity in their manufacture and use, it is here pointed out that the dynamitards and anarchists are liable to fail from the difficulty of manufacturing a safe article without an amount of care not easily secured when the process is carried on illegally. It is, however, to be again remembered that the dangers of ill-made dynamite do not always fall upon the guilty parties. It may be asked whether the economy of time and labour from the use of the high explosives in place of gunpowder, is a sufficient compensation for the destruction of life and property attending upon their employment.

Other ably-written and luminous chapters treat of the coal-tar colours, of photography, of indiarubber and its transformations, of chemical manures, of aerated water, and of disinfectants and germicides.

Few of the outside public, even of the so-called "intelligent and respectable classes," can read these chapters without having their eyes opened, literally and, even still more, figuratively. It might, of course, have been briefly pointed out that our disgraceful inferiority in the manufacture of the coal-tar colours is due to the joint action of two causes; the fact that our students instead of being trained in discovery, are compelled to waste their time and energies in "preparing for exams.," and, secondly, to the laxity of our laws, which allow an alien to hold a British patent without attempting or intending to put it in use on British soil.

The work before us merits the warmest recommendation.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxx., No. 25, June 24, 1895.

Further Studies on the Fluorescence of Argon and on its Combination with the Elements of Benzene. —M. Berthelot. (See p. 13).

On the Lactones or Campholenic Olides.—MM. Berthelot and Rivals.—It results from the author's researches that the lactones have formation-heats notably superior to those of the isomeric acids; the deviation measured between the liquid acid and the inactive lactone being $143.8 - 131.7 = +12.1$.

Solution of Neutralisation Heats of the Campholenic Acids.—M. Berthelot.—The author has determined the heats of the liquid and solid campholenic acid and of campholic acid.

Reduction of Silica by Charcoal.—Henri Moissan.—M. Moissan has obtained a very decided reduction by heating a mixture of rock-crystal and of carbon in powder in a cylinder of coke closed at one end. If the temperature is not very high a part of the silicon escapes the action of the carbon, and is found in the state of crystals or of fused globules. This procedure may be applied to the preparation of silicon by refrigerating its vapour at the moment of production.

Condensation-products of Valeric Aldehyd (Methyl 2-Butanal-4). Observations concerning the Paper of Barbier and Bouveault.—C. Friedel.—The author has been for some time engaged with a study of the condensation-products of valeric aldehyd by the action of dilute soda, aqueous or alcoholic. One of these products is the substance which Barbier and Bouveault regard as dimethyl-26-heptene-3-methylal-3, and which they have further condensed with acetone.

Properties of Solid Carbonic Acid.—P. Villard and R. Jarry.—Dry carbonic acid was distilled and solidified in a wide refrigerated tube in which a thermometer had been introduced axially. The melting-point of the solid acid was -56.7° . The pressure at the time was 5.1 atmospheres. The point of refrigeration was then observed and found to be -56.7° at the pressure of 5.1 atmospheres. This result agrees substantially with the figures found by Faraday. The point of ebullition of solid carbonic acid is at -79° . Regnault found -78.16 and Pouillet -79° . Ether mixed with solidified carbonic acid (carbonic snow) does not reduce the temperature. Methyl chloride behaves quite differently: setting out from -65° the carbonic snow dissolves without liberation of gas, and at the moment of complete saturation the thermometer marks -85° . The lowest temperature reached by means of carbonic snow *in vacuo* is -115° , a point which was maintained for nearly three hours.

On a Formula of M. Guye.—A. Colson.—Referring to a paper by Guye and Jordan (*Comptes Rendus*, p. 1274) the author holds that the simplified formula of Guye is unfounded, and that the direction of the rotatory power is not indicated in a satisfactory manner by a formula founded solely upon chemical hypotheses.

On the Alcohols Derived from a Dextro-Tersben-thene, Eucalyptene.—G. Bouchardat and Tardy.—An attentive study of the derivatives of the various natural terebenthenes with different rotatory powers will probably enable it to be established that these carbides are merely mixtures of two active turpentine, dextro- and levorotatory, meeting each other in variable proportions.

Condensation of the Non-saturated Aldehyds of the Fatty Series with Dimethylacetone; Synthesis of Aromatic Hydrocarbons.—Ph. Barbier and L. Bouveault.—The authors consider the condensation of methylacroleine with acetone and the condensation of α -isopropyl- β -isobutylacroleine with dimethylketone.

Double Combinations of the Nitriles belonging to the Fatty Series acid to the Aromatic Series with Aluminium Chloride.—G. Perier.—This memoir is not adapted for useful abridgment.

Action of Air upon the Must of Grapes.—V. Martinand.—Of all the elements of must the red soluble colouring matter is the most readily oxidisable. In grapes of the type of the Petit-Bouschet there exists a colouring matter oxidisable by air, and one which is less so or not

at all, and which does not hinder the action of the air from proceeding upon the other elements of the must. The bouquet of wine is due not only to the bouquets which exist pre-formed in the grape and to those developed during the fermentation, but also, in some varieties, to the elements contained in the must. The colouration of white wines and their taste are due to an oxidation of the must, and are not derived from fermentation. It is possible to prepare white wines with black grapes by extracting the total juice which they can yield, and submitting it, before fermentation, to the following operations:—Refrigeration to check fermentation, aération to precipitate the colouring matter, and, lastly, filtration of the liquid to prevent its re-colouration during fermentation.

Treatment of the Bites of Venomous Serpents by Chloride of Lime and by Anti-venomous Serum.—A. Calmette.—MM. Phisalix and Bertrand erroneously ascribe to the author a view which he repudiates, i. e., that chloride of lime has a vaccinal action. Conclusive experiments with chloride of lime have been made successfully upon human subjects, especially by Prof. Halford, at Melbourne. He is now sending out immunising serum in considerable quantities to India, the Antilles, and Australia. It is sufficient to inject into rabbits a dose of the serum equal to 1-10,000th of their weight to enable them to bear afterwards, without danger, a dose of venom capable of killing check specimens in from three to four hours.

MISCELLANEOUS.

Institute of Chemistry.—The following Candidates have passed the Examinations for Membership, July 2nd to July 5th, 1895:—*For the Fellowship*: Fuerst, Alexander Frankenbacher (Ph.D., Heidelberg), The University of Heidelberg. *For the Associateship* (under Regulations in force prior to October 1st, 1893): Andrews, Ernest Robert, Finsbury Technical College; Barnes, Charles Kepler, University College, Liverpool; Bodey, Augustus Charles, University College, Bristol, and Pharmaceutical Society's Research Laboratory; Bowie, James Girdwood, Mason College, Birmingham; Bowles, Horace Edgar, Finsbury Technical College; Buchanan, John, Glasgow and West of Scotland Technical College; Burbridge, James Kerry, King's College, London; Desch, Cecil Henry, Finsbury Technical College; Dodd, Frederick Robertson, Glasgow and West of Scotland Technical College, and Registered Student under A. Smetham, Esquire, F.I.C.; Guthrie, Thomas, Yorkshire College, Leeds; Hill, Charles Alexander, Pharmaceutical Society's Research Laboratory, and King's College, London (Physics); Hirst, Henry Reginald, Yorkshire College, Leeds; King, Herbert, Yorkshire College, Leeds; Meggitt, Loxley, University College, Nottingham; Ridding, Howard Charles (Assoc. R.S.M.), Royal College of Science, London; Warden, John Blair, Glasgow and West of Scotland Technical College, and School of Mines, Freiberg; Wharton, Frederick Malcolm, Mason College, Birmingham; Woollatt, George Henry, University College, Nottingham, and Royal College of Science, London. *Final Examination for the Associateship* (New Regulations): Robins, Walter (B.Sc. Lond.), Finsbury Technical College.

NOTES AND QUERIES.

*. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Wanted, a Respirator.—Can any reader supply the name of maker of a respirator suitable for wear in the laboratory? Protection is desired against entrance of hydric sulphide into the lungs either by mouth or nose.—*ASPHYXIA*.

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THE CHEMICAL NEWS.

VOL. LXXII., No. 1862.

A POSSIBLE COMPOUND OF ARGON.

By WILLIAM RAMSAY, F.R.S.

THERE are three ways of forming an endothermic compound. First, by choosing such a reaction as shall on the whole give rise to heat-evolution; as when potassium hypochlorite is produced by passing chlorine into a solution of caustic potash; water and potassium chloride are produced simultaneously with great heat-evolution, so that the algebraical sum of heat is positive. A second method is to use the silent discharge; and by this means oxygen can be oxidised into ozone. A third method depends on the fact that an endothermic compound is more stable at high than at low temperatures, and that if it can be suddenly withdrawn from a hot region a certain proportion, at least, will escape decomposition. By this means acetylene can be produced by causing an arc to play in an atmosphere of hydrogen.

The first of these methods would appear to be impossible with argon. No definite compound is known; much less one produced with heat-evolution.

The second method has been used apparently with some success by M. Berthelot.

The third method has recently been tried; and though much remains to be done, circumstances render it desirable that I should record in a preliminary note certain results which I have recently obtained.

The arc was made *in vacuo* between two thin carbon rods, enclosed in a globular bulb; this was in order to expel, to a certain extent at least, occluded gas. The bulb was then filled with argon, and placed in communication with a graduated reservoir of dry argon. After some four hours, in which the pressure was always somewhat above that of the atmosphere, so that leakage inwards could not have occurred, all was allowed to cool. The volume of the gas had increased by about one-fifth. No alteration of volume was caused in this gas on exposure to water, to caustic soda, or to ammoniacal cuprous chloride; hence the gas contained no carbonic anhydride or oxide. The spectrum of this gas, while showing a faint argon spectrum, exhibited a very finely channelled spectrum, so luminous as to give the impression of a continuous spectrum, together with certain lines which are not coincident with argon lines, judging by a careful comparison in which both spectra were in the same field. Mr. Crookes has kindly undertaken to examine the spectrum, and will doubtless report on it.

Further experiments will be made; but I must content myself at present with chronicling the few facts which I have observed.

University College, Gower Street,
July 26, 1895.

OPENING UP SILICATES BY MEANS OF PURE LEAD CARBONATE.

By P. JANNASCH.

THE first chemist who made a successful attempt to decompose silicates quantitatively by fusion with lead oxide was, G. Bong (*Zeit. f. Anal. Chemie*, xviii., p. 270). Subsequently W. Hempel and R. F. Koch (*Ibid.*, xx., p. 496) gave the preference to bismuth oxide. Recently I had the opportunity to experience the advantages of the use of lead oxide when effecting the analysis of some specimens of topaz in concert with H. Jas. Locke. The many

experiments which I have lately made on incinerating and weighing lead- and bismuth-oxides in platinum vessels, induced me to attempt the opening up of silicates by direct mixture with pure lead carbonate and subsequent fusion in a platinum crucible. From these very successful experiments there originated the following general procedure for the analysis of silicates.

The requisite chemically pure lead carbonate is suitably obtained by precipitating a hot solution of lead acetate with the calculated quantity of ammonium carbonate.

The granular precipitate obtained is first washed in a tall beaker by repeated decantation, then distributed on several rapid filters (made by Desaga, of Heidelberg) *not folded filters*, perfectly washed with boiling waters, finally with suction, carefully removed from the paper without injuring it, and finally completely dried in a capacious porcelain capsule at the heat of the water-bath and with stirring.

For opening up silicates I use a large thick-sided platinum crucible, of 52 to 53 m.m. in height, 45 m.m. in width at the top, and weighing, together with its cover, 72 grms. We thus obtain better melts, and most completely avoid the volatilisation of traces of alkali.

For effecting the fusion we put into the crucible from ten to twelve times the quantity of dry lead carbonate, add the very finely pulverised and air-dried specimen (which has been weighed in a small tube), and mix thoroughly with the glass rod, and heat the whole—under cover, at first gradually, approaching the crucible with a flame of an inch in height for about fifteen to twenty minutes, whereby the greater part of the carbonic acid escapes; it is then more strongly heated to fusion at redness, but only about one-third of the height of the crucible must be actually red-hot. It is remarked that if the silicate contains organic matter, this must be first destroyed by gentle ignition before admixture with lead carbonate. It is also stated that the platinum crucible is less attacked than by a fusion with sodium carbonate or an alkaline hydrosulphate.

Care must be taken to use a thoroughly non-luminous flame, so as completely to obviate any action of reductive gases upon the contents of the crucible. After fusion for ten to fifteen minutes the crucible, when as glowing hot as possible, is plunged into cold distilled water, displacing the cover of the crucible by the tongs as little as possible. To prevent the projection of any small particles of the melt, with the aid of tapping the bottom of the crucible and gentle pressure of the sides, the cake of melt is caused to fall into a large flat Berlin capsule, corresponding quantities of pure concentrated nitric acid and hot water are added, and the whole is evaporated down on the water-bath, continually comminuting all the fragments of the melt as they are gradually disintegrated add softened, until there remain at last more or fewer light-coloured flocks of silica floating in the liquid. In the meantime the residue of the melt, which forms only a slight coating in the crucible, is placed, along with water and some strong nitric acid, in a boiling water-bath, and after a short time the solution obtained, including some silica, can be mixed with the chief quantity. The saline mass, after being sharply dried on the water-bath, is again moistened with at least 20 to 25 c.c. of concentrated nitric acid, and again evaporated down until as dry as dust. This residue when cold is moistened with 10 c.c. concentrated nitric acid, allowed to stand at rest for ten minutes, and then mixed with from 750 to 1000 c.c. of water, heated for fifteen minutes on the water-bath, and filtered from the silica, which is finally most carefully washed with boiling water, to which at first a little nitric acid is added.

The filtrate from the silica is mixed in the cold with a large excess of concentrated hydrochloric acid, in order to separate the bulk of the lead as a chloride, which, after subsidence, is then filtered with suction and washed with cold hydrochloric acid (1 vol. concentrated acid and 1 vol. water). This filtrate is again evaporated to dryness in a

capacious capsule, especially for the complete expulsion of any free nitric acid. The residue is mixed with 30 c.c. dilute hydrochloric acid (1 : 4), and as much water heated on the water-bath for fifteen minutes and allowed to cool, when any residual traces of lead chloride are collected upon a very permeable filter, and quickly washed with cold water. The resulting filtrate now contains unimportant quantities of lead, which are finally quantitatively precipitated with hydrogen sulphide. To this end the gas is first introduced in the cold; it is then heated for some time until the lead sulphide has settled, and the liquid is finally allowed to cool in a current of sulphuretted hydrogen.

The precipitate, which is generally slight, is filtered off and washed with warm water, to which fresh sulphuretted hydrogen water is constantly added. Above all, care must be taken that the precipitation of the lead is really complete, as otherwise the further course of the analysis will be disturbed in the most troublesome manner, or inaccurate results will be obtained.

Then from the filtrate free from lead all hydrogen sulphide must be removed, by concentrating the solution before the iron is oxidised, by means of nitric acid or hydrogen peroxide, on undertaking the general procedure for separating iron, alumina, manganese, lime, magnesia, potash, and soda.

I have already had several analyses of rocks executed by a number of my pupils according to the above method, which agreed in their results most satisfactorily with the combined results of sodium carbonate fusion and opening up with hydrofluoric acid.

After further elaboration of the lead oxide method for the case of the simultaneous presence of titanium and phosphoric acid, I propose communicating all the analytical material in connection. I cannot sufficiently extol the use of lead carbonate in the analysis of silicates. As compared with the former methods, it means a very considerable economy of time, and it need fear no comparison with them as regards the accuracy of the results.—*Zeit. Anorgan. Chemie*, viii., p. 364.

NOVEL REACTIONS OF MORPHIA.

By G. BRUYLANTS.

ON heating morphia or one of its salts in a steam-bath with a little pure concentrated sulphuric acid, and adding a drop of Fröhde-Buckingham reagent (1 c.grm. molybdate to 1 c.c. of acid), there is produced a splendid green colour, which lasts for some time and then disappears.

This reaction is almost as sensitive as the Fröhde reaction properly so called. It seems to me to have some importance, because we see the same reagent produce two distinct reactions with the same substance placed in different conditions, and also because this green colouration is characteristic of other alkaloids of opium.

To produce it we heat, for two or three minutes, the watch-glass on which we have placed the morphia and the sulphuric acid, then spread out a drop of the mixture on

a plate of white porcelain, and add a drop of the reagent.

We may combine the lilac reaction of Fröhde, the green colouration and the reaction of Huseman, when operating on the same product. To this end we dissolve the morphia on a watch-glass in one or two drops of sulphuric acid. We spread out a part on the porcelain, and add an equal quantity of Fröhde's reagent, obtaining thus the lilac colour. Then we heat the watch-glass in the steam-bath, take a fresh portion of the mixture, and with a further quantity of the reagent we obtain the green colouration. Having observed this, we introduce into the liquid while still green a grain of nitre, when we immediately see the green tint give place to a red colour, which grows paler in time, and lastly turns yellow.

I take this opportunity to remark that it has been erroneously recommended to heat the mixture of morphia and sulphuric acid in the steam-bath for half an hour, to obtain Huseman's reaction; one or two minutes will be sufficient. Whatever may be the purity of the acid and the morphia, there always is produced, after heating for half an hour, a violet colour more or less intense,—a colouration which, in fact, has no influence upon the ulterior reaction with nitre when it is required to identify pure morphia. But it is no longer the same case if the morphia has been extracted from some part of a dead body in the course of a toxicological investigation. It is then always more or less contaminated with foreign matters which sometimes colour the test-liquid in a very intense manner, so that it becomes very difficult to seize upon the play of colours produced by the nitre.

If we heat the product only for one minute or two minutes, the mixture is very slightly coloured, and is very suitable for the reaction.

I arrange below, in a table, the colours produced by morphia and some of the other bases of opium, by the action of Fröhde's reagent on a solution of morphia in sulphuric acid before and after being heated in the steam-bath, as well as the colours produced by the addition of nitre to the product of the last operation.

II. It is known that, on adding an aqueous solution of iodic acid to a solution of morphia in sulphuric acid, there is produced a deposit of iodine. On adding iodic acid to the sulphuric solution of morphia previously heated in the steam-bath, we obtain, according to the proportions, a lilac which turns slowly to red and then disappears, or else a red at once. The former result is with a trace of iodic acid, the second is with a large proportion of that reagent. This character has some importance.—*Bulletin de la Soc. Chimique*, Series 3, xiii.-xiv., No. 9, p. 498.

ATOMIC WEIGHTS OF NICKEL AND COBALT.

By CLEMENS WINKLER.

THE author has undertaken a revision of the atomic weights of nickel and cobalt, with the object of ascertaining which of the two has the higher atomic weight.

Kind of Alkaloid.	I. Fröhde's Reagent on the Sulphuric Solution before heating.		II. Fröhde's Reagent on the Sulphuric Solution after heating.		III. As in II., followed by the addition of a grain of Nitre.	
	Lilac colour.		Green colour.		Green colour, changes to red, which fades and disappears.	
Morphia	Lilac colour.		Green colour.		Green colour, changes to red, which fades and disappears.	
Apomorphia	Green-blue.		Do.		Do.	
Oxidomorphia	Blue.		Do.		Violet, turning to red.	
Cocleia	Dirty green, then blue.		Do.		As morphia.	
Narceia	Brown, turning to green and then to blue.		Dirty green.		Do.	
Narcotina	Green, then greenish-brown.		Green.		Violet, then a fugitive red.	
Papaveria	Green, then blue and then red.		Green, then blue and red.		Green colour, disappears once.	
Maconia	Green, very fugitive.		Greenish blue.		Do.	
Cryptopia	Dirty green, then brownish- green.		Dark green.		Do.	

The experiments were effected by treating the metals with a solution of auro-potassium bromide, dissolving the metals in hydrochloric acid, determining the hydrogen evolved, treatment with solution of iodine in excess, and titrating back the excess of iodine.

The average of the determinations showed, for nickel, the value 58.7155; and for cobalt, 59.3678.

The author thinks that these figures must be accepted as the true atomic weights of nickel and cobalt, referred to $H=1$ and $I=126.53$.—*Zeit. Anorg. Chemie und Chem. Zeitung.*

RECENT ANALYSES OF LEUCITE BASALT FROM VESUVIUS.

By ALBERT THORPE.

I HAVE recently analysed samples of leucite basalt from Vesuvius, and the following results may be of interest to the readers of the CHEMICAL NEWS, as Vesuvius is now in a state of eruption.

	I.	II.
Silica	47.23	47.32
Alumina	18.23	18.00
Ferric oxide	4.21	4.23
Ferrous oxide	4.49	4.31
Manganous oxide	1.36	1.42
Lime	8.63	8.51
Magnesia	4.68	5.03
Potash	8.00	7.92
Soda	2.63	2.70
Titanic acid	0.23	0.36
Phosphoric acid	0.31	0.20
	100.00	100.00

The specific gravities of the basalt varied from 2.653 to 2.721.

ON CERTAIN PHENOMENA OBSERVED IN THE PRECIPITATION OF ANTIMONY FROM SOLUTIONS OF POTASSIUM ANTIMONYL TARTRATE.*

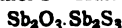
By J. H. LONG.

(Concluded from p. 45).

Reaction with Sodium Thiosulphate.

COLD dilute solutions of the thiosulphate and potassium antimonyl tartrate can be mixed without immediate precipitation. Application of heat, however, produces a light yellow precipitate, which grows deeper and finally becomes bright red. This precipitate is the substance commonly known as antimony cinnabar, used as a pigment, and on the large scale is made by decomposing the thiosulphate by antimony chloride. In the reaction between the thiosulphate and tartar emetic the precipitate appears very heavy, but the decomposition is far from complete, as shown by the figures given below.

There seems to be some doubt as to the composition of this precipitate. Roscoe and Schorlemmer (ii., Part 2, 324) give it as, probably, Sb_2S_3O ; referring, however, to other formulæ. Dammer's "Handbuch" gives—



as the probable formula. Others are also given. Recently, Baubigny (*Comptes Rendus*, No. 17, 1894) has given reasons why the formula Sb_2S_3 should be considered the correct one, and the proof he presents appears to be satisfactory. There remains a possibility, however, that the composition may, under certain circumstances, vary with the method of preparation. In fact, some of my own re-

sults seem to show this, and I am now engaged in studying the question further. But, as made in the reaction in hand, the composition seems to be $2Sb_2S_3 \cdot H_2O$. This was determined by the following considerations:—The precipitate dissolves in hydrochloric acid without liberation of sulphur, yielding a perfectly clear solution. A solution made in this way was heated, mixed with a little tartaric acid solution, and precipitated by hydrogen sulphide in the usual manner. On filtering off the orange-yellow precipitate so obtained in a Gooch crucible, drying at 120° , and weighing, the weight was always found less than that of the antimony cinnabar taken.

Sulphur determinations were made by dissolving a gram. or less of the substance in strong S-free solution of potassium hydroxide, and then oxidising the sulpho-salt formed by washed chlorine gas (method of Rivot). The results of these tests were as follows:—

	Calculated for $2Sb_2S_3 \cdot H_2O$.	Found.
Sb	69.56	69.80
S	27.83	27.72

No determination of the water was made, but its presence was shown in the substance dried at 120° by heating to a higher temperature in a narrow glass tube.

In a series of experiments on the precipitation a number of portions of the tartrate, of 5 grms. each, were weighed out and dissolved in 150 c.c. of water. Varying amounts of the thiosulphate in 50 c.c. of water were added, and then water enough to make exactly 250 c.c. The flasks holding the mixtures were closed with perforated stoppers containing long glass tubes, and then heated in the water-bath one hour. In this way evaporation was practically avoided. At the end of the hour the precipitates were collected on a Gooch funnel, dried at 120° , and weighed with the following results:—

No. of experiment.	Weight of $Na_2S_2O_3 \cdot 5H_2O$ added. Grms.	Weight of precipitate. Grm.
1.	0.1	0.0039
2.	0.2	0.0068
3.	0.4	0.0111
4.	0.8	0.0178
5.	1.6	0.0363
6.	3.2	0.0803
7.	6.4	0.2112
8.	12.8	0.4809

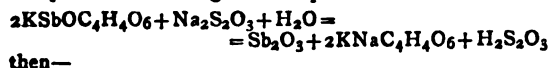
In a second set of tests I dissolved, in each case, 10 grms. of the tartar emetic in 100 c.c. of hot water and added the thiosulphate in 50 c.c. of hot water. The mixtures were kept at 100° two hours and then filtered. Results as follows:—

No. of experiment.	Weight of $Na_2S_2O_3 \cdot 5H_2O$ added. Grms.	Weight of precipitate.
9.	5	0.1915
10.	10	0.4041
11.	15	0.5162
12.	20	0.6818

It is evident from these figures that in both sets of experiments the reaction is far from complete and not easily determined. It is, perhaps, quite complex. I noticed in no case the escape of hydrogen sulphide or sulphurous oxide, and the gradual change in colour during precipitation from very light yellow to bright red suggests that it takes place in two stages. Vortmann (*Ber. d. Chem. Ges.*, xxii., 2307) has studied the general problem of decomposition of thiosulphuric acid, and states that it breaks up into H_2S , O , and SO_2 . In presence of certain metals, tetra- and pentathionates seem to be formed. It is certain that no sulphate is formed in the reaction in hand, but the proof of formation of the several thionic acids is difficult because of the incompleteness of the reaction and the presence of the great excess of thiosul-

phate. In cases of complete reaction, however, Vortmann and Vaubel, also (*Ber. d. Chem. Ges.*, xxii., 2703), have shown that these acids are formed.

I suggest, therefore, this explanation of the present reaction. At the outset there may be, as with borax, a decomposition according to this equation—



then—



the oxygen and sulphur dioxide being held, however, to form polythionates.

The gradual change of colour can be accounted for by the gradual change of oxide into sulphide of antimony, and it seems possible that under certain conditions of concentration and temperature a part of the oxide should remain unchanged, accounting for the results of some of the analysts who have examined the precipitate. In several instances I modified the experiment by mixing warm solutions of the tartar emetic with warm thiosulphate solutions, and then throwing the mixture into a large volume of cold water the instant a precipitate began to form, to check the reaction. The precipitate which now settled was very light coloured instead of red, and appeared to be a mixture of oxide and sulphide. The microscopic appearance of this precipitate is distinctly different from that of the antimony cinnabar.

As explained at the outset, some time elapses after mixing cold solutions before a precipitate appears. In the beginning of the interval the solution may be so clear that accurate polarimetric observations are possible. But, contrary to expectations, based on the behaviour in other cases recorded, I find the specific rotation of the tartar emetic, in this stage of the reaction, quite unchanged. After precipitation a marked decrease was observed as usual. This is shown in the following table in which the filtrates from the last precipitates referred to were made up to 250 c.c. before polarisation:—

No. of experiment.	Thiosulphate added. Grms.	α_D observed.	α_D calculated.
9.	5	10°90'	10°89'
10.	10	10°43'	10°46'
11.	15	10°07'	10°24'
12.	20	9°69'	9°93'

In the last column the rotations were calculated on the assumption that antimony is precipitated and Rochelle salt formed according to the last equations. In the eleventh and twelfth experiments the thiosulphate is present in amount much in excess of that necessary to complete precipitation by these reactions, and it is evident that a decomposition of the active molecule has taken place not indicated by the amount of precipitate.

There seems to be a fundamental difference between the reaction with the thiosulphate on the one hand, and those with the borate, carbonate, phosphate, acetate, and tungstate on the other. In the first case we appear to have no breaking up of the complex tartrate until actual precipitation occurs, while in the others the stages are quite distinct. I have shown that in these last reactions acids are liberated which may be readily recognised. It is also true that these acids are practically without action on antimonous oxide, from which it would follow that this substance might remain a long time, possibly in the hydrated form, in contact with the liberated acids without change. This would not be the case with liberated thiosulphuric acid. If set free in the presence of antimonous oxide, even the dry precipitate, it soon converts it into sulphide. Any cause, therefore, which acts to destroy the equilibrium in the solution of tartrate and thiosulphate must lead to the almost immediate formation of a precipitate.

In many of our most familiar cases of precipitation the formation of the precipitate is so rapid that we are accus-

tomed to look upon it as instantaneous. But by varying the conditions of precipitation it may be shown that even the reaction between barium chloride and sulphuric acid is one which consumes an appreciable interval. In such cases, however, we have no means of knowing what takes place before the precipitate becomes actually visible. It is, doubtless, true that the liquid regarded as supersaturated for BaSO_4 does not begin to throw this out in solid form until a relatively large number of these molecules combine to produce a particle of a certain size, but at what rate the Ba and SO_4 ions combine cannot be shown.

But in the cases before us we have evidence, first, of the gradual breaking up of the complex potassium antimonyl tartrate, and then, also, that a relatively large amount of the antimony may be separated before any of it falls as a precipitate. The stage of precipitation seems to follow as a perfectly distinct and also progressive one. It is hastened, as in other cases of supersaturation, by heat or agitation. One of the reactions shows, also, that a relatively long time is consumed in combination as well as in dissociation. In the case of the mixture containing the tartrate and tungstate we have evidence of the splitting of the first molecule, and then, from the slowly increasing rotation, evidence of the addition of an element from the second to the active part of the first. Both of these phenomena are observed before precipitation appears.

It must be remembered that the several acids shown to be liberated in these experiments are all so-called weak acids, or acids but slightly dissociated in solutions. It is also true, as a test of their electric conductivities shows, that the solutions of tartar emetic are relatively little dissociated (see in this connection Hugo Haedrich, *Zeit. Phys. Chem.*, xii., 496). There is doubtless, therefore, a close connection between the phenomena outlined above, and others depending on the degree of dissociation of the ions in solution. A study of the behaviour of weaker solutions would doubtless lead to interesting results not brought out in the above experiments which were undertaken mainly to show the character and amount of precipitates formed. A discussion of the behaviour of dilute solutions will follow.

A REVISION OF THE ATOMIC WEIGHT OF STRONTIUM.

FIRST PAPER: THE ANALYSIS OF STRONTIC BROMIDE.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 43).

The Ratio of Silver to Strontic Bromide.

First Series.—In this series a slight excess of silver was taken, dissolved, and diluted with at least a hundred times its weight of water, and added to the strontic bromide in glass-stoppered flask. After the usual long-continued shaking, the precipitate was collected upon a Gooch crucible, and the excess of silver in the evaporated filtrate and first five or six wash waters was determined after Volhard's method (*Proc. Amer. Acad.*, xxix., 66). Upon subtracting this small excess of silver from the total, the amount corresponding to the strontic bromide remains. This method is not a very satisfactory one, the final result being probably too low, because of loss of a portion of the slight excess of silver.

Second Series.—Here the end point of the reaction was determined by titration after the method of Abraham (*Proc. Amer. Acad.*, xxviii., 24), very weak solutions of silver and hydrobromic acid being used to titrate barium and forwards. The mean reading was taken in each case, and the method of procedure resembled exactly that work with barium. These results are much more tr-

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy*.

worthy than the last. In several cases the sample of strontic bromide was first analysed by this method, and subsequently an excess of silver nitrate was added and the preceding method was applied.

Third Series.—For this series a new method was devised. According to Stas (*Mém. de l'Acad. Belg.*, xliii., Part ii., Introduction), argentic bromide is wholly insoluble in water; according to Goodwin (*Zeit. f. Phys. Chem.*, xiii., 645), it is only very slightly soluble; while according to Kohlrausch and Rose (*Zeit. f. Phys. Chem.*, xii., 234), it is soluble to the extent of three-tenths of a milligramme in a litre. The time during which chloride of silver is shaken makes an enormous difference in the solubility, and it is not impossible that a similar effect may occur here. Perhaps Kohlrausch and Rose did not agitate their precipitate so thoroughly as Stas did. According to the present experience the purest silver bromide was capable of yielding a filtrate which would give a very faint opalescence with both silver and hydrobromic acid; and this effect usually diminished upon long continued agitation. The method of determination used in this series was based upon this fact. Somewhat less silver than the amount

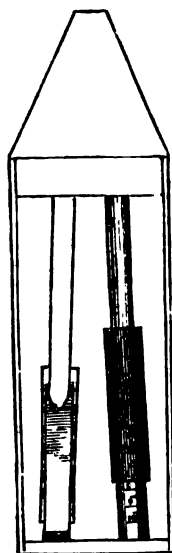


FIG. 3.

required was added to the strontic bromide, and a very weak standard solution of argentic nitrate (the cubic centimetre contained a milligramme of silver) was dropped in until equivalent solutions of silver and hydrobromic acid produced equal opalescence in two similar pipetted portions of the supernatant liquid. Since the opalescence was so faint that one could only with difficulty see it at all under ordinary conditions, a piece of apparatus which may be named a "nephelometer" (*νεφέλη*, a cloud), was devised for detecting it. Two test-tubes, holding each just 30 c.c., were arranged in a wooden frame so that 2 centims. of the top of the tubes were in darkness. The bottoms of the tubes were fitted into the top of larger opaque tubes containing water, and were provided with closely fitting cylindrical shades, which could be raised or lowered independently over a graduated scale. All these contrivances prevented disturbing side reflections from the meniscus at the top of the tube and the rounded glass at the bottom. The two test-tubes were slightly inclined towards one another, so that the eye at a distance of 8 inches could look directly into both without change of position. Filled with pure water the tubes appear absolutely black, even when exposed to a strong light; but an

absurdly small amount of precipitate, which no ordinary means could discover at all, makes a very evident cloudiness. By sliding the shades up and down a point may be found where the two tubes, containing solutions of different cloudiness, appear equal in depth of tone. The reason of this is that only the portion of the opalescence is visible upon which light is allowed to fall. Of course the intensities of the opalescence, and hence the quantities of precipitate, are then inversely as the length of the lighted portions of the two tubes.

If care is taken to direct the light horizontally upon the tubes, considerable accuracy may be obtained with the apparatus, especially if the columns are nearly equal in cloudiness.

A pointed blackened roof with a small hole in the top for the eye is useful in excluding light from the surface of the liquid, thus rendering the comparison easier. The chief advantages in the apparatus lie in the facts that the two disks of light to be compared remain equal in size throughout the comparison, and that the eye is not confused by bright surface reflections. Two typical test series are given below. In each case one shade was adjusted at 10 centims. and the other was run backward and forward until apparent similarity was obtained.

(a). One tube contained 0.010 m.grm. of silver, and the other 0.0125 m.grm., measured by means of a very dilute standard solution. Both amounts were made up to 25 c.c., and 1 c.c. of hundredth normal hydrochloric acid was added to each. The opalescence in each was then compared after a thorough stirring and a short delay.

Heights of Columns appearing Alike.

Stronger Solution.	Weaker Solution.
C.m.	C.m.
8.7	10.0
7.9	10.0
6.9	10.0
7.6	10.0
8.4	10.0
8.6	10.0
8.9	10.0
Found .. 8.1	10.0
True value 8.0	10.0

(b). In a similar experiment one tube contained 0.025 m.grm. of silver, the other 0.0225 m.grm.

Heights of Columns appearing Alike.

Stronger Solution.	Weaker Solution.
C.m.	C.m.
8.8	10.0
8.9	10.0
8.2	10.0
9.5	10.0
8.9	10.0
8.7	10.0
8.9	10.0
9.4	10.0
Found .. 8.9	10.0
True value 9.0	10.0

Some series were more accurate, others less so, than these, which serve to give a fair idea of the probable error of the method.

The details of the analysis must be evident from what has been said. The method is similar to Stas's third method for the determination of chlorine (*Proc. Amer. Acad.*, xxix., 86), except that of course the opalescence is very much fainter.

Below are given the tables containing the data and results of the three series; these will be comprehensible without further remark.

Ratio of Strontic Bromide to Silver.

First Series. Volhard's Method.

No. of Anal. Sp.	No. of Strontic Bromide taken.	Weight of Silver taken.	Total Weight of Silver.	Weight of Silver of corres. to Strontic Bromide.	Ratio SrBr ₂ Ag ₂	Atomic Weight Sr.
		Grms.		M.g.		
1. III.	1'49962	1'30893	1'38	1'30755	114'689	87'658
2. III.	2'41225	2'10494	1'43	2'10351	114'677	87'633
3. III.	2'56153	2'23529	1'72	2'23357	114'683	87'645
4. V.	6'15663	5'3686	0'2	5'3684	114'683	87'644
	12'63003			11'01303	114'683	87'644

Ratio of Strontic Bromide to Silver.

Second Series. Abrahall's Method.

No. of Anal. Spec.	No. of Strontic Bromide taken.	Weight of Silver required.	Ratio SrBr ₂ Ag ₂	At. wt. of Strontium.
	Grms.	Grms.		
5. III.	1'49962	1'30762	114'683	87'645
6. III.	2'41225	2'10322	114'693	87'667
7. III.	5'24727	4'57502	114'694	87'668
8. V.	6'15663	5'3680	114'691	87'663
	15'31577	13'35386	114'692	87'663

Third Series. New Method.

9. IV.	2'9172	2'5434	114'697	87'675
10. VI.	3'8946	3'3957	114'692	87'665
11. VI.	4'5426	3'9607	114'692	87'664
12. III.	5'2473	4'5750	114'695	87'671
	16'6017	14'4748	114'694	87'668

(To be continued.)

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 20th, 1895.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

(Concluded from p. 48).

92. "On some Physical Properties of the Chlorides of Gold." By T. K. ROSE, D.Sc., A.R.S.M.

The melting-point of trichloride of gold is found to be 288° C., under a pressure of about two atmospheres of chlorine. Its density is 4'3, and that of the monochloride, 7'4. These determinations tend to show that the atomic volume of chlorine when in combination with gold is 4×5'1, instead of 3×5'1, the volume assigned to it by Schröder in the case of some of its other compounds. Mr. W. J. Pope found that volatilised crystals of trichloride of gold are crystalline aggregates, but that they cannot be referred to any system as they do not transmit the light from a sodium flame.

93. "The Dissociation of Liquid Nitrogen Peroxide. Part II. The Influence of the Solvent." By J. TUDOR CUNDALL.

The author measures colorimetrically the dissociation at different temperatures of solutions of nitrogen peroxide in fourteen "indifferent" solvents, viz.:—Chloroform, ethylene chloride, ethylidene chloride, methylene chloride, carbon tetrachloride, benzene, monochlorobenzene, monobromobenzene, ethyl bromide, ethylene bromide, bromoform, silicon tetrachloride, carbon disulphide, and acetic acid. He finds that the dissociation takes place in the same way, though to a different extent, in the various solvents; the extent of dissociation at any temperature

being in the main an additive property, though probably modified by constitution. Thus the carbon atoms in a compound have very little influence on the dissociation power; those of hydrogen have more; then those of bromine and chlorine, whilst those of sulphur and silicon have most. Ethylene chloride is not so effective as ethylidene chloride.

The author compares his results with those of Mentschutkin (*Zeit. Phys. Chem.*, i., 611, and vi., 187) and brings evidence to show that, if the heat of dissociation of liquid nitrogen peroxide is the same as that calculated by van't Hoff for the gas, any reaction that may take place between the dissolved substance and "indifferent" solvent is probably not exothermic.

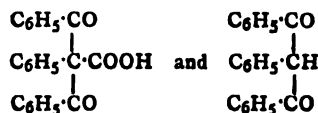
94. "Condensation of Benzil with Ethylic Acetoacetate." By FRANCIS K. JAPP, F.R.S., and G. DRUCE LANDER, B.Sc.

By heating a mixture of benzil and ethylic acetoacetate with sodium ethoxide in alcoholic solution, the two first-mentioned compounds condense according to the equation $2C_{14}H_{10}O_2 + C_6H_{10}O_3 = C_{34}H_{28}O_6 + H_2O$. This condensation product is obtained as a sodium compound containing alcohol of crystallisation: $C_{34}H_{27}NaO_6 \cdot C_2H_5O$. Acetic acid liberates from this compound ethylic anhydrodibenzilacetoacetate, $C_{34}H_{28}O_6$, which crystallises from alcohol or from a mixture of ethylic acetate and light petroleum in flat needles or prisms, with bevelled edges, melting with decomposition at 210–211°. Although this compound contains the carbethoxyl group, it was not found possible to hydrolyse it to the corresponding acid, owing to the ease with which it is decomposed with regeneration of benzil.

By boiling this compound with alcohol containing a little sulphuric acid ethylic ethylanhydrodibenzilacetoacetate, $C_{34}H_{27}(C_2H_5)O_6$, was obtained, which was deposited from alcohol in slender prisms melting at 197°. It was readily hydrolysed by caustic potash. Ethylanhydrodibenzylacetoacetic acid, $C_{32}H_{23}(C_2H_5)O_6$, is deposited from benzene in microscopic matted needles melting at 216°. It is isomeric with the condensation compound.

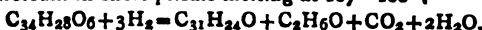
Substituting isobutylic for ethylic alcohol in the foregoing etherification, ethylic isobutylanhydrodibenzilacetoacetate, $C_{34}H_{27}(C_4H_9)O_6$, was obtained. It crystallised from a mixture of benzene and light petroleum in minute needles, melting at 202°. On hydrolysis it yielded isobutylanhydrodibenzilacetoacetic acid, $C_{32}H_{23}(C_4H_9)O_6$, which was deposited from a benzene solution in slender needles melting at 237°.

When the condensation compound was oxidised with chromium trioxide in acetic acid solution it yielded a monobasic acid, $C_{22}H_{16}O_4$, which crystallised from a mixture of ethylic acetate and light petroleum in needles melting at 200° with evolution of carbon dioxide. In this process of decomposition by heat the acid is converted into a compound $C_{21}H_{16}O_4$, which is deposited from alcohol in needles melting at 119–120°. The constitution of these two compounds may possibly be expressed by the formulæ—



Phenyldibenzoylacetic acid. Phenyldibenzoylmethane.

Fuming hydriodic acid at its boiling-point converts the condensation product into a compound $C_{31}H_{24}O$, which crystallises from a mixture of ethylic acetate and light petroleum in short prisms melting at 187–188°.



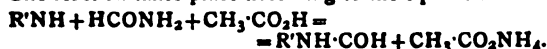
Suspecting that the condensation product was a carbethoxyl derivative of anhydronedibenzil (Japp and Miller, *Trans.*, 1885, xlviii., 34), the authors reduced the latter compound with boiling hydriodic acid, and obtained

the foregoing reduction compound $C_{31}H_{24}O$ (m. p. 187—188°) together with an isomeric crystallising from a mixture of ethylic acetate and light petroleum in pyramids melting at 155—159°.

The results do not permit of a conclusion being drawn as to the constitution of the condensation product. The constitution of anhydrazetonedibenzil is also unknown.

95. "On a Method for Preparing the Formyl Derivatives of the Aromatic Amines." By H. R. HIRST and J. B. COHEN, Ph.D.

Formamide reacts with the aromatic primary amines in presence of cold glacial acetic acid, forming formyl derivatives. The mixture is allowed to stand for a few hours, and the product poured into water. The resulting derivative is nearly pure, and the yield is very satisfactory. The reaction takes place according to the equation—



The secondary aromatic amines containing an alkyl radicle only react on heating, whereas the tertiary amines and diphenylamine do not react even after continued boiling.

The formyl derivatives of the following bases have been prepared:—Aniline, ortho- and para-toluidine, α - and β -naphthylamine, phenyl- and orthotolyl-hydrazin, methyl- and ethyl-aniline, paraphenylenediamine, and benzidine.

96. "A Modification of Zincke's Reaction." By H. R. HIRST and J. B. COHEN, Ph.D.

A small piece of aluminium foil coated with mercury, which is prepared by dipping the foil into a solution of mercuric chloride, is capable of bringing about a reaction between benzyl chloride, chloroform, &c., on the one hand, and aromatic hydrocarbons on the other. This reaction closely resembles that of Zincke, but takes place at the ordinary temperature. With benzyl chloride and benzene a satisfactory yield of pure diphenylmethane may be obtained. In a similar manner phenyltolylmethane and phenylxylylmethane have been prepared.

97. "A Method for Preparing Cyanuric Acid." By W. H. ARCHDEACON, B.Sc., and J. B. COHEN, Ph.D.

When urea in fine powder is heated in a sealed tube with the calculated quantity of phosgene in 20 per cent toluene solution, little action occurs until the temperature rises above 180°. A tube which had been heated for four hours at 170—180° showed very little pressure on opening; but after being re-sealed and heated for seven hours at 190° and eight and a half hours at 230°, great pressure was observed on opening the tube, and hydrochloric acid fumes were copiously evolved. The brownish microcrystalline product was separated by filtration and dried *in vacuo*. It amounted in two experiments to 133 and 127 per cent of the urea used. It dissolved without change in cold concentrated sulphuric acid, being re-precipitated in a crystalline form by water. It dissolved also in alkalis, and from the neutral solution in ammonia silver nitrate threw down a white amorphous precipitate.

The characteristic needles of the sodium salt, and the amethyst-coloured precipitate with copper ammonium sulphate solution, served to identify the compound as cyanuric acid.

The crude product gave the following result on analysis:—

I. 0.095 grm. gave 28.2 c.c. nitrogen at 17° and 737 m.m.
II. 0.1753 grm. gave 0.040 grm. H_2O and 0.179 grm. of CO_2 .

Theory for $(CONH)_3$.		Found.
C	27.91	27.85
H	2.33	2.53
N	32.56	33.38

The reaction probably occurs according to the equation
 $3CO(NH_2)_2 + 3COCl_2 = 2(CONH)_3 + 6HCl$.

98. "The Oximes of Benzaldehyd and their Derivatives." By C. M. LUXMOORE, B.Sc.

The paper contains an account of experiments under-

taken with a view to throwing further light on the isomerism of the aromatic aldioximes. As already mentioned in a preliminary note by Professor Dunstan and the author (*Proc. Chem. Soc.*, 1893, 253), in examining the mechanism of the change of benzantialdoxime into benzsynaldoxime by hydrogen chloride, the previously unknown benzantialdoxime hydrochloride has been isolated; on solution it is converted into the syn-hydrochloride. The two isomeric sulphates have also been prepared. Since the change of the antioxime into its isomeric is always preceded by the formation of a derivative of the former, which then passes into the more stable syn-derivative, a stereo-chemical explanation of the isomerism is rendered probable.

By the action of methyl bromide on benzantialdoxime the hydrobromide of its "nitrogen" methyl ether is produced (m. p. 67°). This ether yields the same products of hydrolysis and reduction as the "nitrogen" methyl ether obtained from benzsynaldoxime. It differs from the latter in its lower melting-point and in the extreme readiness with which it is hydrolysed. The hydrobromide is stable, but the ether itself rapidly passes on standing into the isomeric syn-nitrogen ether. Structural formulae are insufficient to explain the existence of the four isomeric ethers (two "oxygen" and two "nitrogen") which are known. Probably, therefore, the aldioximes themselves are stereo-isomeric; but both act tautomerically, and the synaldoxime reacts more readily in the sense of the isoximido formula than the antialdoxime does.

Treated with phosphorus pentachloride both oximes yield a little formanilide, but chiefly benzonitrile. Phosphorus trichloride converts benzantialdoxime into an extremely unstable chlorine derivative; with benzsynaldoxime it yields benzonitrile and hydrogen chloride instantaneously.

Almost all the stereo-chemical hypotheses equally well explain the isomerism of oximido-compounds of triad nitrogen; but in the case of derivatives with pentad nitrogen Pickering's theory is more in accordance with the facts than any other.

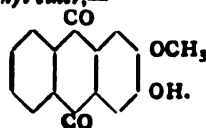
99. "On a Colouring-matter from 'Lomatia ilicifolia' and 'Lomatia longifolia'." By EDWARD H. RENNIE, M.A. (Sydney), D.Sc. (Lond.).

The author describes a yellow colouring-matter adhering to the seeds of two different species of *Lomatia*, a plant belonging to the order Proteaceae. The colouring-matter is easily extracted by hot water, and is regarded by the author as *hydroxylapachol*. Its barium derivative closely resembles the barium derivative of hydroxyhydrolapachol described by Hooker. When treated with sulphuric acid under certain conditions, it is converted into *hydroxy- β -lapachone*. Other derivatives are described in the paper, and also an isomeric *hydroxylapachol*.

100. "The Colouring and other Constituents contained in Chay Root." Part II. By A. G. PERKIN and J. J. HUMMEL.

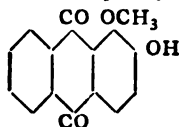
A previous examination of chay root (*Trans. Chem. Soc.*, 1893, 1160) showed that it contained rubichloric acid, two waxes, cane-sugar, ruberythric acid, alizarine, two dimethyl ethers of anthragallol (A) and (B), m. p. 209°, and 225—227°; an alizarine monomethyl ether, and *m*-hydroxyanthraquinone. By the investigation of very large quantities of the root, 2 cwts., obtained through the Imperial Institute, two new substances have been isolated.

One substance, $C_{15}H_{20}O_4$, was obtained as orange-coloured needles melting at 232°. When heated with hydrochloric acid to 180° it yielded hystazarin, and was found to contain one methoxyl group. It is therefore an *hystazarinmonomethyl ether*.—



A second constituent, $C_{16}H_{12}O_5$, formed minute orange-red needles melting at $212-213^\circ$, and its acetyl compound at 160° . It contained two methoxy groups, and by the action of hydrochloric acid at 180° was converted into anthragallol. It was consequently an anthragallol dimethyl ether, and it is interesting to note that chay root therefore contains the three dimethyl ethers of anthragallol.

Since the publication of the previous communication (*loc. cit.*), Schunck and Marchlewski (*Trans. Chem. Soc.*, 1894, 182) have prepared the alizarine β -monomethyl ether from alizarine. This is not identical with that found in chay root, which must consequently be the α -compound,



The readiness with which this is decomposed into alizarine by boiling with dilute alkalis, readily accounts for its non-production by the usual methods.

101. "The Six Dichlorotoluenes and their Sulphonic Acids." By W. P. WYNNE and A. GREEVES, Assoc. R.C.S.

Sulphonic derivatives of the 1:2:5- and 1:3:4-dichlorotoluenes were described in a previous paper (*Trans. Chem. Soc.*, 1892, 1050, *et seq.*); the present communication deals with the remaining isomerides and their sulphonic acids.

1:2:3-Dichlorotoluene was prepared by three methods: (a) from 1:2:5-nitrothotoluidine by chlorination, (b) from Lellman and Wüthner's 1:2:3-nitracetothotoluidide (m. p. 158° , *cf. Annalen*, ccxxviii., 239), and (c) from orthochlorotoluenesulphonic acid by nitration. It boils at $207-208^\circ$ under 760 m.m. pressure, and on oxidation yields a dichlorobenzoic acid melting at 164° (*cf. Seelig, Annalen*, ccxxvii., 162). On sulphonation two isomeric acids are obtained, which can be separated by means of their barium salts. The acid from the less soluble barium salt forms a very soluble chloride, crystallising in radiate needles, melting at 45° , and an amide, melting at 221° , whilst that from the more soluble barium salt is the 1:2:3:5-derivative, and like this yields a chloride, crystallising in well-defined prisms, melting at 85° , and an amide, melting at 185° .

1:2:4-Dichlorotoluene was prepared (a) from metatolylendiamine by Erdmann's method (*Ber.*, xxiv., 2769), (b) from 1:2:4-nitrothotoluidine, and (c) from orthochlorotoluenesulphonic acid by nitration. It boils at $199-200^\circ$ under 760 m.m. pressure. On sulphonation, it yields the 1:2:4:5-acid, characterised by the chloride crystallising in elongated scales, melting at 71° , and the amide, melting at 177° .

1:2:6-Dichlorotoluene was prepared from the 1:2:6-nitrothotoluidine of Green and Lawson (*Trans. Chem. Soc.*, 1891, 1013). It boils at $199-200^\circ$ under 760 m.m. pressure, and on oxidation yields a dichlorobenzoic acid melting at 139° (*cf. Claus and Stavenhagen, Annalen*, cclxix., 228). On sulphonation, an acid is obtained which gives a chloride, crystallising in prismatic needles, melting at 60° , and an amide, melting at 204° .

1:3:5-Dichlorotoluene was prepared from the 1:3:4:5-dichloroparatoluidine by Lellmann and Klotz's method (*Annalen*, ccxxii., 321) and from the 1:2:3:5-dichlorothotoluidine of Claus and Stapelberg (*Annalen*, cclxiv., 292). It boils at $201-202^\circ$ under 760 m.m. pressure. On sulphonation, an acid is obtained which forms a very soluble chloride, melting at 45° , and an amide, melting at 168° .

To aid in the determination of the constitution of the dichlorotoluenesulphonic acids, the nitro-derivatives of the five known chlorotoluenesulphonic acids have been prepared and examined. For example, 1:2:4-orthochlorotoluenesulphonic acid on nitration gives as chief

product the 1:2:4:5-nitro-acid, since the dichlorotoluenesulphonic acid obtained from it is identical with that obtained from 1:2:5-dichlorotoluene (*Trans. Chem. Soc.*, 1892, 1052). In like manner, 1:2:5-orthochlorotoluenesulphonic acid is shown to give as chief product the 1:2:4:5-nitro-acid, and as subsidiary product the 1:2:3:5-nitro-acid.

1:2:3-Nitrothotoluidine is converted by Sandmeyer's method into the nitrothochlorotoluene, which boils at 263° under 760 m.m. pressure. On reduction, this yields the 1:2:3-orthochlorometatoluidine, which boils at $228-229^\circ$ under 760 m.m. pressure, and forms an acetyl derivative melting at 132° .

1:2:4-Nitrothotoluidine in like manner yields the nitrothochlorotoluene, which crystallises in pale yellow needles, melting at 65° , and the orthochloroparatoluidine, which boils at 245° under 760 m.m. pressure, and forms an acetyl derivative melting at 86° .

1:2:5-Nitrothotoluidine on chlorination in the presence of iodine yields a chloronitrothotoluidine melting at 168° . This is the 1:2:3:5-derivative, since, by eliminating the NH_2 -radicle, it forms the 1:3:5-nitrochlorotoluene melting at 61° , the 1:3:5-chlorometatoluidine, characterised by its acetyl derivative melting at 151° (*cf. Honig, Ber.*, xx., 2419), and 1:3:5-dichlorobenzoic acid melting at 182° . By Sandmeyer's method the corresponding nitrodichlorotoluene, which crystallises in pale yellow needles melting at 83° , was obtained, and from this, by reduction, the dichlorometatoluidine, which crystallises in needles, melts at 88° , boils at 292° under 760 m.m. pressure, and forms an acetyl derivative melting at 187° .

1:2:6-Nitrothotoluidine yields a chlorothotoluidine, which boils at 245° under 760 m.m. pressure, and forms an acetyl derivative melting at 154° .

The mixture of dichlorotoluenes obtained by chlorinating orthochlorotoluene under Seelig's conditions (*loc. cit.*) is being examined with the object of determining its constituents.

102. "The Disulphonic Acids of Toluene and of Ortho- and Parachlorotoluene." By W. P. WYNNE and J. BRUCE, Assoc. R.C.S.

As is known (*cf. Trans. Chem. Soc.*, 1892, 1082), parachlorotoluene, on sulphonation, forms a product containing both the 1:2:4- and 1:3:4-sulphonic acids. Experiments have been undertaken with the object of estimating the relative proportions of these acids, both directly and by an examination of the disulphonic acids obtained by sulphonating parachlorotoluene with 20 per cent anhydrosulphuric acid. For the purposes of comparison, chloroacids have been prepared by Sandmeyer's method from the paratoluidinemono- and di-sulphonic acids of known constitution.

The paratoluidinedisulphonic acids obtained by Richter from the 1:3:4- and the 1:2:4-paratoluidinemono-sulphonic acids (*Annalen*, ccxxx, 314, 331) are shown to be the 1:3:4:6- and 1:2:4:6-derivatives respectively. The former, by elimination of the NH_2 -radicle, gives a toluenedisulphonic acid identical with that obtained from the 1:2:5-orthotoluidinesulphonic acid by the xanthate method.

1:2:4-Parachlorotoluenesulphonic acid, prepared from the corresponding amido-acid, gives a sparingly soluble barium salt, a chloride melting at $23-24^\circ$, and an amide melting at 142° . On sulphonation with 20 per cent anhydrosulphuric acid, it yields, as sole product, an acid identical with that obtained from the 1:2:4:6-paratoluidinedisulphonic acid.

1:3:4-Parachlorotoluenesulphonic acid, obtained from the corresponding amido-acid, gives an easily soluble barium salt, a chloride crystallising in plates melting at 54° , and an amide melting at 154° . On sulphonation with 20 per cent anhydrosulphuric acid, two disulphonic acids are obtained, the chief product being the 1:3:4:6-derivative, since it is identical with the acid obtained from the 1:3:4:6-paratoluidinedisulphonic acid.

Parachlorotoluene, on sulphonation with 20 per cent anhydrosulphuric acid under similar conditions, gives a mixture of the 1 : 2 : 4 : 6. and 1 : 3 : 4 : 6-disulphonic acids in the proportions of about three parts of the former to one of the latter.

The 1 : 2 : 3 : 5-orthotoluidinedisulphonic acid prepared by Hasse's method (*Annalen*, ccxxx., 286), and shown to be identical with Hasse's product by conversion into the bromotoluenedisulphonic chloride, gives, by the hydrazine method of eliminating the NH_2 -radicle, a toluenedisulphonic acid, which differs from that described by Hasse, since its chloride (Cl found 24.5, Hasse 25.9, theory 24.6) melts, not at 132° , but at 95° .

1 : 2 : 5-Orthochlorotoluenesulphonic acid gives, on further sulphonation, a product which seems to differ from that obtainable from Hasse's acid by Sandmeyer's method, and is being further examined.

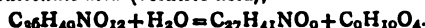
In addition to the known 1 : 2 : 4., 1 : 2 : 5., and 1 : 3 : 5-toluenedisulphonic acids, the following have been prepared :—

1 : 2 : 6-Toluenedisulphonic acid, obtained from the 1 : 2 : 4 : 6-paratoluidinesulphonic acid, by eliminating the NH_2 -radicle, forms a potassium salt crystallising with $\frac{1}{2}\text{H}_2\text{O}$ in minute prisms, and a chloride, crystallising in scales, melting at 99° .

1 : 3 : 4-Toluenedisulphonic acid, obtained from the 1 : 3 : 4-paratoluidinemetasulphonic acid by the xanthate method, forms a mono-hydrated potassium salt crystallising in needles, and, on treatment with phosphorus pentachloride, yields the chloride, which crystallises from benzene with $\frac{1}{2}$ mol. proportion of benzene in large prisms melting at about 60° , and from petroleum spirit in scales melting at 111° .

103. "Contributions to our Knowledge of the Aconite Alkaloids." Part XII. "The Constitution of Pseudoaconitine. Preliminary Notice." By WYNDHAM R. DUNSTAN, F.R.S., and FRANCIS H. CARR.

Pseudoaconitine is the name given by Alder Wright to the highly toxic alkaloid contained in Nepaul aconite (*Aconitum ferox*). It is a crystalline base, melting at $104-105^\circ$, whose composition is expressed by the formula $\text{C}_{36}\text{H}_{49}\text{NO}_{12}$. When hydrolysed it furnishes, according to Alder Wright and Luff (*Trans. Chem. Soc.*, 1878), pseudoaconitine and one molecular proportion of dimethylprotocatechuic acid (veratric acid),—



The authors are engaged in a re-investigation of this alkaloid in the light of their recent work on the constitution of aconitine derived from *Aconitum napellus* (*Trans. Chem. Soc.*, 1894, 176, 290).

The pseudoaconitine employed by the authors was extracted from the roots of *Aconitum ferox*, some of which were provided by the Government of India through the Imperial Institute. The highly-purified crystalline base melted at 201° , that is, nearly 100° higher than the point recorded by Wright and Luff; this melting-point was not changed by fractional crystallisation.

When heated slightly above its melting-point, pseudoaconitine loses a molecular proportion of acetic acid, leaving a new base, which it is proposed to name *pyropseudoaconitine*. This alkaloid, on hydrolysis, loses a molecular proportion of dimethylprotocatechuic acid, furnishing *pyropseudoaconitine*.

On complete hydrolysis with alkali, pseudoaconitine yields, in addition to the dimethylprotocatechuic acid observed by Wright and Luff, a molecular proportion of acetic acid, which was identified and estimated in the manner described in the authors' previous paper on aconitine.

When pseudoaconitine sulphate is heated in a closed tube with water, it suffers, like aconitine, partial hydrolysis, the acetyl group alone being eliminated, producing a molecular proportion of acetic acid. In this action a new alkaloid is formed, corresponding with the benzacanine derived in a similar manner from aconitine, which

the authors propose to name *veratrylpseudoaconitine*. This substance is a crystalline base (m.p. 181°) which, when hydrolysed, furnishes pseudoaconitine and dimethylprotocatechuic acid (veratric acid).

There is therefore a close resemblance between the constitution of aconitine and of pseudoaconitine, both alkaloids undergoing hydrolysis in a similar manner. The molecule of each alkaloid contains an acetyl group; but in pseudoaconitine the benzoyl group of aconitine is replaced by the veratryl group, aconitine being *acetylbenzaconitine*, and pseudoaconitine *acetylveratrylpseudoaconitine*. As far as the authors' investigation has proceeded, pseudoaconitine appears to be distinctly different from the aconine derived from aconitine. There is little reason at present to doubt that the crystalline highly active alkaloid isolated by the authors is identical with Wright's pseudoaconitine, but further evidence on this point is being obtained.

Library.

The Library will be closed during the last fortnight in August for cleaning and the annual revision of the Catalogue. Fellows are requested to return all books in their possession not later than August 15th.

Research Fund.

The following grants have been made by the Council on the recommendation of the Research Fund Committee :—

- £30 to Messrs. J. J. Hummel and A. G. Perkin, for the investigation of certain natural colouring-matters.
- £10 to Dr. H. Ingle, for the purchase of various aldehydes, ketones, and hydrazine, to continue his work on stereoisomeric osazones.
- £10 to Dr. J. J. Sudborough, to continue his work on diortho-substituted benzoic acids.
- £15 to Mr. E. Haworth, for the synthesis of an acid having the composition $\text{C}_8\text{H}_{14}(\text{COOH})_2$, and the comparison of its properties with those of camphoric acid.
- £5 to Mr. R. E. Doran, for a research on the preparation of mustard oils by the reaction of chloro-carbonic esters with lead thiocyanate.
- £15 to Dr. W. A. Bone, to continue a research on the substituted succinic acids, and on the behaviour of various trimethylene compounds on treatment with the sodium compound of ethylic malonate.
- £10 to Dr. B. Lean, to extend his work on the derivatives of ethylic butane tetracarboxylate.
- £20 to Dr. J. Walker, for an investigation of the conditions of equilibrium between the cyanates and the corresponding ureas.

NOTICES OF BOOKS.

The Mechanical Auxiliaries of Chemical Technics. ("Die Maschinellen Hilfsmittel der Chemischen Technik"). By A. PARNICK, Civil Engineer, formerly Head-Engineer at the Griesheim Chemical Works. With 337 Illustrations. Frankfurt-on-Mayn: H. Bechold. 1894. 8vo., pp. 320.

THAT a work of this character should have been found requisite is a striking proof of the development of the chemical industries in Germany. It is now found necessary that the technical chemist should possess a clear and comprehensive acquaintance with the mechanical auxiliaries which he has to employ. On the small scale in the laboratory, the skilled hand of the chemist brings into mutual contact in their due proportions and conditions the substances which have to react. But when we transfer the process from the laboratory to the works, and employ hundred-weights in place of grms., there arises a new task.

Mechanical auxiliaries have to be devised which may take the place of the skilled hand, and on their presence or absence, or rather on their perfection or defectiveness, the whole question of success or failure may turn.

To take an instance. The ammonia-soda process was invented and patented in Britain long before the days of Solvay. But the mechanical appliances for carrying out the reaction were so imperfect that the process was a commercial failure until better appliances were devised by Solvay and his coadjutors, when ammonia-soda became a formidable rival to the Leblanc process. Other similar cases might readily be found, and it will strike the reader that reactions have been conceived which remain a dead-letter because the arrangement and construction of the proper plant has presented difficulties not yet surmounted.

Hence the technical chemist, without seeking to become a jack-of-all-trades, ought to have a general acquaintance with the appliances used for the various types of chemical processes, so that he may select such as are likely to suit his exact purpose. He must be able to come to an understanding with the mechanical engineer, and to explain precisely what he wants. Hence the work before us, compiled as it is by an experienced specialist, will be of great service to graduates of universities and polytechnics on their entrance into a practical career.

After a few useful generalities, the author treats systematically of sources of power, of the transmission of power, and of contrivances for the conveyance of material products. Under this last heading is included the removal of offensive or pernicious vapours. These, it is said, are not to be conveyed into the soil, though the author, very questionably, seems to sanction their direct introduction into water.

The fourth section discusses machines for comminution, including disintegrators, indigo-mills, and colour-mills. Mixing machines are described adapted for solids alone, liquids alone, and for incorporating solids with liquids and gases.

Next follow appliances for fusion, solution, and lixiviation, for concentration and vaporisation, for mechanical separations (including extraction and fractionation). Here are included filter-presses, appliances for separation by crystallising, by sublimation, and by refrigerating machines.

Mention is made of the increasing preference shown for the ammonia process as compared with the use of carbonic acid.

Desiccatory apparatus forms the subject of the ninth chapter, and in the tenth we have an account of apparatus for determining weight, temperature, pressure, and draught of gaseous current. An instrument devised by Arndt bears the remarkable name of the "econometer," and is here figured. It consists of a gas balance depending on a novel principle, and fixed in an air-tight case. The illustrations of the work are not only numerous, but for the most part very well drawn. Many of them, however, have a very annoying fault; the lettering is done, not with printing characters, but with script, and to make matters worse, with German script. As instances we may mention Figs. 202, 203, 224, &c. This is the more remarkable as the larger portion of the illustrations are lettered in a rational manner with printing characters.

How Shall Young Men be Educated in Applied Chemistry?
By P. T. AUSTEN, Ph.D., F.C.S., Professor of Chemistry in the Brooklyn Polytechnic Institute.

CONCERNING this essay we may say that, in part, Prof. Austen's advice to students is exceedingly judicious, and his demands thoroughly rational. But in part it must be confessed that his requirements are exorbitant, leading merely to a waste of time and of brain-power. What must be thought, e.g., of the following programme? "A thorough grounding in history, the elements of law,

political economy, metaphysics, logic, ethics, and literature should be effected." We submit that to the man of science history, other than the history of discovery and invention and their treatment by the world, is little better than fossil gossip; political economy and metaphysics must rank as a waste of time. The same should be remarked concerning mere ratiocinative logic, ethics, and literature. The elements of law are admissible merely as far as patents and sanitary regulations are concerned. On other matters, and on general principles, in as far as such can be said to exist, the technical chemist may well be referred to solicitors and counsel, remembering that his opinion on legal questions will only be received by the courts with derision.

The technical chemist will, of course, require to be well grounded in physics, especially in thermotics, optics, and electricity. Nor should mathematics be overlooked; but, on the principle of the division of labour, the "business side of industrial chemistry" had better be left to book-keepers and accountants.

A knowledge of the German and French languages is, of course, indispensable.

Much more useful to the technical chemist than metaphysics, ethics, and literature, will be botany and zoology. He may often be called upon to study the applicability of newly-discovered animal or vegetable products and the ways of combatting new parasites.

The author gives also moral lessons. The young works-chemist is told to be "honest to a fault"—an expression difficult to understand. He certainly should not cook results, but for telling the whole truth and nothing but the truth he may earn scant gratitude. We could point out a chemist who in his young days got into dire disgrace for reporting the presence of a serious percentage of arsenic in a sulphur ore just taken into stock, and was cautioned in future to determine nothing in the ores but sulphur, copper, and silver. If we, in turn, may give a piece of advice, we would caution every young technical chemist to shun any industrial establishment where a "self-made man" is in course of formation.

An excellent recommendation given by Prof. Austen is that the more advanced students in technical chemistry should not merely seek to make new substances by well-known methods—as is largely done, especially in Germany—but should be practised in producing known substances by new methods.

The author's essay abounds in suggestions of the highest importance, but we are led to question whether in these days the chemical student, if trained on his lines, would not be overwhelmed with matter of very secondary value.

University of Wyoming, Laramie, Wyoming. Departments of Chemistry and Mechanical Engineering. Special Bulletin. January, 1895. The Heating Power of Wyoming Coal and Oil; with a Description of the Bomb Calorimeter. By EDWIN E. SLOSSON, Professor of Chemistry, and L. C. COLBURN, Professor of Mechanical Engineering.

THE authors give a table of the heating-power of Wyoming coal, and its proximate analysis. They discuss the varied efficiency of bodies, mentioning that only from 45 to 85 per cent of the theoretical evaporation power is actually obtained.

The Wyoming mineral oils are said to possess nearly double the heating capacity of the coals from the same region. The oils are said to be much like the Baku oils.

The methods of determining heating-power are next considered. Concerning the boiler test it is admitted that approximately accurate results can be obtained only from an experimental plant. The disadvantages are that the experiment is always a test of the efficiency of the furnace and boiler, and of skill in firing, rather than a determination of the absolute value of the fuel.

Elementary chemical analysis is a tedious and delicate

process, the rather as the carbon may exist in different states which have not identical heats of combustion.

The authors recognise calorimetry as the most satisfactory method of determining the heating-power of a fuel. For this purpose they prefer the apparatus of Mahler, a cheaper modification of the celebrated bombe calorimétrique of Berthélot. Mahler's instrument is described and figured, and the corrections necessary in its use are given.

Year-Book of Organic Chemistry. Edited by GAETANO MINNUMI, of Palermo. Vol. I., 1893. With a Preface by ERNST VON MEYER. Large 8vo., pp. xiv. and 882. Leipzig: J. A. Barth. 1895.

THE author endeavours to collect in a single volume all newly-observed facts in organic chemistry, the results both of experiments and speculation. The volume for 1893 has already appeared, and that for 1894 will, it is hoped, be issued in the course of the present year.

CHEMICAL NOTICES FROM FOREIGN SOURCES

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxi., No. 1, July 1, 1895.

At the meeting of July 1st Herr Schwarz was elected a correspondent of the Section of Geometry, *vice* the late Neumann; Baron Müller was elected a correspondent of Botanical Section, *vice* the late Fringsheim; and Dr. Engelmann was elected a correspondent of the Section of Medicine and Surgery, *vice* Herr Heidenhain.

This issue contains a short obituary notice of Professor Huxley, a correspondent of the Section of Anatomy and Zoology.

Determination of Small Quantities of Arsenic.—Ad. Carnot.—This paper will be inserted in full.

Oxidation Products of Benzyliden-camphor and of Benzyl-camphor. Nitrosate and Nitronitrite of Benzyliden-camphor. —A. Haller. —If benzyliden-benzyl-camphor are submitted to the action of oxidising agents they are ruptured at the point of attachment of the aromatic radicle, and the two nuclei behave then in the oxidising medium as if they were free.

On Paratungstic Acid.—L. A. Hallopeau.—It is easy to obtain solutions of paratungstic acids presenting all the known reactions of the paratungstates, and becoming converted into metatungstic acid on ebullition, just as the paratungstates are transformed into metatungstates. Paratungstic acid therefore really exists as Laurent maintained, but the little stability of its molecule caused it to be split up into tungstic acid and water on the simple concentration of its solutions. This fact alone distinguishes it from Graham's colloidal tungstic acid, which may be evaporated to dryness and heated to 200° without decomposition.

Determination of Alumina in Phosphates.—Henri Lasse.—This paper will be inserted in full.

On Sodium Amidide.—M. de Forcrand.—A thermochemical paper, not adapted for useful abstraction.

Phosphoric Ethers of Allylic Alcohol. Allylphosphoric Acid. —J. Cavallier. —Allylphosphoric acid has the composition $\text{PO}_4\text{C}_3\text{H}_5\text{H}_2$. With coloured reagents it behaves like most of the oxy-acids of phosphorus. Neutrality with methyl orange is obtained by the addition of 1 mol. of soda and neutrality with phenolphthalein by 2 mols. It forms two series of salts: neutral salts,

$\text{PO}_4\text{C}_3\text{H}_5\text{M}_2$, and acid salts, $\text{PO}_4\text{C}_3\text{H}_5\text{MH}$. The author describes the most important salts of both series.

Preparation and Conductivity of New Cyanomethinic Ethers.—J. Guinchant.—Not admitting of useful abstraction and not of sufficient moment to claim insertion in full.

No. 2, July 8, 1895.

Action of Zinc Chloride upon Resorcine.—E. Grimaux.—The author obtains a substance fusible at 225°. It forms small colourless needles soluble in alcohol, acetone, sparingly soluble in ether, and soluble in 100 parts of boiling water. Its cold watery solution has a blue fluorescence, which is stronger if dissolved in alkalis, in ammonia, or in concentrated sulphuric acid. This substance is identical with umbelliferone, $\text{C}_9\text{H}_6\text{O}_3$. Another substance formed, $\text{C}_{22}\text{H}_{18}\text{O}_3$, is fusible at 264°. It is insoluble in water, soluble in alcohol, acetone, and ether.

Volumes of Salts in their Aqueous Solutions.—Lecoq de Boisbaudran.—This paper requires the accompanying diagram.

On Diphenylanthrone.—A. Haller and A. Guyot.—The researches of the authors show that the compound $\text{C}_{26}\text{H}_{18}\text{O}$ obtained by various procedures enumerated may be considered as diphenylanthrone. As the constitution of this substance is established, we are warranted in attributing to phthalyl tetrachloride, fusible at 88°—a scheme which makes of it a dissymmetric molecule. Phthalyl dichloride contains tetrachloride.

Direct Spectral Analysis of Minerals and of certain Melted Salts.—A. de Gramont.

Determinations of the Solubility of Some Organic Compounds in Carbon Disulphide at very Low Temperatures.—Henryk Arctowski.—This memoir cannot be inserted without the insertion of the complicated diagram of curves.

Certain Oxidising Properties of Ozonised Oxygen, and of Oxygen exposed to the Sun's Rays.—A. Besson.—The author has formerly shown that ozonised oxygen acts upon perchloric ethylene, C_2Cl_4 , forming, as the main product, trichloroacetyl chloride, CCl_3COCl , and as an accessory product carbonyl chloride, COCl_2 . He has since found that the same products are equally formed if dry oxygen is caused to act upon C_2Cl_4 in presence of direct solar light. Ozonised oxygen and dry oxygen, in presence of sunlight, react energetically upon the phosphorus iodides, setting free iodine, and forming complex products containing phosphorus, oxygen, and iodine.

Action of Nitric Oxide upon certain Metallic Chlorides, i.e., Ferrous Chloride and the Bismuth and Aluminium Chlorides.—V. Thomas.—The yellowish brown compound formed from the ferrous chloride corresponds in composition with the compound obtained by saturating a solution of ferrous chloride with nitric gas at temperatures between 12.5° and 25°. Bismuth chloride exposed to the action of nitric oxide takes a yellowish colour, but the reaction is complete only after the lapse of several days. The compound ultimately obtained has the composition $\text{Bi}_2\text{Cl}_6\text{NO}$. The corresponding aluminium compound has the composition $\text{Al}_2\text{Cl}_6\text{NO}$. It has a pale yellow colour. Both the above compounds are highly hygroscopic, and the aluminium compound fumes on exposure to the air.

Action of the Halogens upon Methylic Alcohol.—A. Brochet.—This paper is not adapted for abstraction.

On a Physical Theory of the Perception of Colours.—Georges Darzens.

Revue Universelle des Mines et de la Metallurgie.
Vol. xxx., No. 2.

This issue contains no chemical matter.

MISCELLANEOUS.

Preliminary Researches on the Hydrolysis of the Aqueous Solutions of Mercuric Chloride.—Henryk Arctowski.—The author has the ultimate purpose of expounding our entire knowledge on the chemical action of water upon salts. For the present he restricts himself to the case of mercuric chloride.—*Zeitschrift für Anorg. Chemie.*

Preservation of Wheat.—M. Balland.—The author, quoting Duhamel du Monceau, mentions an experiment made on 94 cubic feet of wheat of the crop of 1743, which he had preserved for more than six years with the sole precaution of occasional ventilation, and which was not in the least impaired. Parmentier mentions that in 1774 the King and the royal family tasted bread made of wheat which had been kept for 221 years, and which had been deposited in the citadel of Metz since 1523. The method of preservation is not mentioned.—*Comptes Rendus*, cxx., No. 25.

City and Guilds of London Institute.—The Diploma of "Associate of the City and Guilds of London Institute" has been conferred by the Council of the Institute upon the following matriculated students, who have this year successfully completed the full course of instruction at the Central Technical College:—

Civil and Mechanical Engineering.—H. S. Andrewes, F. G. Arnould, J. E. Chapman, H. E. Fenwick, C. S. Hainworth, E. W. Hainworth, B. H. M. Hewett, E. W. Hummel, F. T. W. Lewis, F. E. Morgan, R. E. Reeves, H. Robinson.

Applied Physics and Electrical Engineering.—J. M. Barr, S. Beeton, C. Brandeis, W. M. Carver, A. D. Constable, S. Gifford, F. S. Grogan, A. C. Hanson, G. S. Hewett, C. D. Le Maistre, P. G. Phelps, W. Reilly, W. Roberts, H. G. Solomon, R. J. J. Swann, C. P. Taylor, E. L. Thorp, E. L. Webb, N. J. Wilson.

Applied Chemistry.—W. G. Bennett, W. A. Davis, W. T. Gidden, C. Revis, E. M. Rich, P. Spencer.

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THE CHEMICAL NEWS.

VOL. LXXII., No. 1863.

A SCHEME FOR QUALITATIVE ANALYSIS OF A SOLUTION CONTAINING HYDRIC SULPHIDE, HYDROSULPHIDE, SULPHIDE, POLY- SULPHIDE, THIOSULPHATE, SULPHITE, AND SULPHATE.

By W. P. BLOXAM, B.Sc. (Lond.).

In the *CHEMICAL NEWS* (lxvii., p. 39) there appears a communication from R. G. Smith, B.Sc., entitled "The Detection of Sulphates, Sulphites, and Thiosulphates, in Presence of Each Other." In this communication the author provides for the detection of sulphates, sulphites, and thiosulphates, and in conclusion states that "Hydro-sulphuric acid would interfere with these reactions, and ought to be eliminated by bubbling carbon dioxide through the solution until the gas escaping from the tube no longer darkens lead-paper."

Without offering further criticism than that the presence of hydric sulphide vitiates entirely any attempt to separate sulphate, sulphite, and thiosulphate, whilst the method recommended for its removal is tedious, an outline of process is here given which has proved satisfactory in dealing with solutions containing normal sulphides, polysulphides, hydrosulphide, free hydric sulphide, sulphite, sulphate, and thiosulphate.

The necessity for such a process arose in the course of an investigation of the products of decomposition, on air exposure, of the laboratory agent known either as ammonium sulphide or ammonium hydrosulphide. The results of this investigation were communicated to the Chemical Society on June 15th, 1893, the paper being entitled "The Sulphides and Polysulphides of Ammonium." An abstract of this paper appeared in the *Proceedings of the Chemical Society*, Oct. 19th, 1893. The paper appeared at length in the *Journal of the Chem. Soc. Trans.* (lxvii., April, 1895). In it the following statement occurs (p. 278):—"The first point was to determine what ammonium compounds, other than sulphide and polysulphide, were present, and this involved the removal of sulphide and polysulphide, and the recognition in the filtrate of sulphite, thiosulphate, and sulphate. A scheme for separation is given by Fresenius ('Chemical Analysis—Qualitative,' translated by C. E. Groves from the 15th German Edition, p. 194), but it was found to require modification before successful results could be obtained, owing to the difficulty of removing the last traces of hydrogen sulphide. An account of the modified method of analysis will appear in another journal."

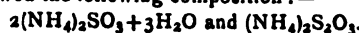
The author had in view publication in the *CHEMICAL NEWS*, and the appearance of Mr. Smith's paper induces him to make good his neglect.

The statement of Fresenius is as follows:—"When, as is often the case, it is required to find sulphites and hyposulphites of the alkalies in presence of alkaline sulphides, solution of sulphate of zinc is first added until the sulphide is decomposed; the sulphide of zinc is then filtered off, and one part of the filtrate is tested for hyposulphurous acid by addition of acid, another portion for sulphurous acid with nitroprusside of sodium, &c."

The treatment prescribed by Fresenius (*Ibid.*, p. 193) for the detection of sulphurous acid is as follows:—"If an aqueous solution of an alkaline sulphite is carefully neutralised with acetic acid, or bicarbonate of soda is added to it, according as it has an alkaline or acid reaction (excess of the bicarbonate is without effect, but excess of

caustic alkali or simple carbonate, or of carbonate of ammonia, prevents the reaction), and a relatively large amount of solution of sulphate of zinc, mixed with a very small quantity of nitroprusside of sodium, be then added, the solution will become red if the quantity of the sulphite present is not too small; when, however, the amount of sulphite is very minute, the colouration makes its appearance only after the addition of some solution of ferrocyanide of potassium. If the quantities are not altogether too minute, a purple-red precipitate will form on the addition of the ferrocyanide of potassium (Bödeker). Hyposulphites of the alkalies do not show this reaction."

Being unable to obtain by purchase ammonium sulphite or ammonium thiosulphate in a state of purity, Mr. W. B. Giles, F.I.C., kindly undertook their preparation, and was eminently successful. Analysis of the pure salts showed the following composition:—



Experiments were made with mixtures of these salts according to the method of Fresenius. It was found, however, that contrary to the statement of Fresenius (*loc. cit.*) the presence of excess of ammonia enhanced the delicacy of the test for sulphite. Experiments demonstrated the possibility of detecting very small traces of sulphite mixed with excess of thiosulphate.

On enlarging the scope of experiments so as to detect sulphite and thiosulphate in a solution containing sulphide and polysulphide, difficulty was experienced in getting rid of the last traces of hydric sulphide by precipitation as zinc sulphite. The solution being treated as recommended with zinc sulphate, and the precipitate removed by filtration, any trace of hydric sulphide left in the filtrate effectually masks the red colouration given by sulphite, the ordinary reaction of sulphides with sodium nitroprusside taking its place; experiments showed that addition of solution of cadmium sulphate would determine the complete removal of hydric sulphide. It was consequently employed in place of zinc sulphate, but the sulphite reaction was not obtained on adding nitroprusside and ferrocyanide. On addition to the filtrate of zinc sulphate, however, the reaction for sulphite was obtained, showing that the presence of cadmium sulphate did not prevent the detection of sulphite, whilst it effected the complete removal of hydric sulphide. Solution of cadmium chloride was employed with similarly successful results, and solution of zinc chloride was successfully substituted for one of zinc sulphate, with a view of eliminating sulphur compounds from the reagents used. Using mixtures of sulphide, polysulphide, sulphite, and thiosulphate, the influence of the following substances on the test was investigated, viz., ammonium chloride, ammonium carbonate, and free ammonia, the results indicating that they did prevent the detection of sulphite. A modified method of testing was accordingly adopted. A mixture of solutions of zinc chloride, cadmium chloride, ammonium chloride, and ammonia, was made in a stoppered cylinder. To this was added the solution containing sulphide, polysulphide, sulphite, and thiosulphate of ammonium. From time to time the mixture was gently agitated, and the air of the cylinder tested with paper moistened with solution of ammoniacal plumbic acetate. When the air was proved free from hydric sulphide, filtration was effected, and a few drops of the clear filtrate tested with solution of ammoniacal silver nitrate. If no colouration or precipitation was observed, the tests for sulphite and thiosulphate were then made. It was found by this method that even very small traces of sulphite could be detected with certainty. Experimenting in this fashion upon laboratory samples of coloured ammonium sulphide, it was determined that they contained thiosulphate, but only traces of sulphite. Under these circumstances it was suspected that during the progress of the test oxidation had taken place, sulphite becoming sulphate. Accordingly the filtrate, after separation of

sulphide and polysulphide, were rendered strongly acid with hydric chloride (free from chlorine), and boiled to expel sulphur dioxide. The deposited sulphur was filtered off, and the filtrate tested for sulphate. Only the slightest traces could be detected, and these were attributed to the imperfect washing of hydric sulphide during saturation of ammonia with gas generated by the action of hydric sulphate on ferrous sulphide.

It being established that oxidation of sulphite did not occur in the course of analysis, experiments were now made upon mixtures containing sulphide, hydrosulphide, polysulphide, sulphite, thiosulphate, and sulphate of ammonium.

The solution was treated as previously described, with the mixture of zinc chloride, cadmium chloride, ammoniac chloride and ammonia, and the filtrate (containing sulphite, thiosulphate, and sulphate) divided into two portions. One portion was treated as previously described for the detection of sulphite and thiosulphate. The other portion was treated as follows, for the detection of sulphate in presence of sulphite and thiosulphate:—The solution, after addition of a small quantity of pure sodic hydric carbonate, was placed in a flask, the cork of which was pierced by three holes. Through an inlet tube a current of washed carbon dioxide was admitted, and an outlet tube was provided dipping below the surface of water. Through the third hole, a small stoppered separating funnel passed, the tube reaching nearly to the bottom of the flask.

Through the cold solution a current of washed carbon dioxide was passed, and the liquid gradually raised to the boil. When all air was expelled, hydric chloride (free from chlorine) was cautiously admitted by the stoppered separating funnel. When excess of acid had been added the solution was boiled down to one-fifth of its original bulk, the current of carbon dioxide being maintained. The concentrated liquid was filtered from deposited sulphur, and a portion of the filtrate tested with ammoniacal silver nitrate to guard against undecomposed thiosulphate. If found to be free the remainder was tested for sulphate.

By these methods mixtures containing sulphide, hydrosulphide, polysulphide, sulphite, sulphate, and thiosulphate, have been successfully treated.

Some experiments have been made with a view to detecting the constituents of mixtures containing polythionates in addition to the sulphur compounds already dealt with, and the results will be communicated to the *CHEMICAL NEWS* in due course.

Royal Naval College, Greenwich, S.E.

PREPARATION OF THIOACETIC ACID, AND ITS IMPORTANCE FOR CHEMICO-LEGAL INVESTIGATIONS.

By ROBERT SCHIFF.

SOME months ago I proposed to abandon, in analytical operations, the unpleasant and tedious use of sulphuretted hydrogen, and to apply in its stead thioacetic acid.

This convenient procedure has hitherto been adopted in but few laboratories, chiefly, as I learn, from the difficulty of preparing large quantities of thioacetic acid by the known methods. The methods of preparation described in chemical literature are all useless. Even that of Kekulé and Linnemann with phosphorus pentasulphide and glacial acetic acid gives enormously bulky black tumid masses, which at once fill the largest vessels, and compel the distillation to be broken off. By the following procedure we may work with any quantity at pleasure.

One part by weight of powdered phosphorus pentasulphide is mixed with $\frac{1}{2}$ part by weight of fragments of glass (not too small) and 1 part of glacial acetic acid, and the

mass is placed in a glass vessel fitted with a thermometer and an ascending condenser, and heated upon the wire gauze with a luminous flame. The reaction begins without any troublesome tumefaction, and is easily regulated by means of the flame.

When the temperature of the vapours has risen to about 103° , the process is interrupted. The yellow product is rectified, and the portion which passes over between 92° and 97° —pure thioacetic acid—is used, either in the free state as a 6 per cent aqueous solution, or as a salt in a 30 per cent feebly ammoniacal solution. We thus obtain pure thioacetic acid amounting almost to one-third of the acetic acid used. For each operation I use in a 2 litre flask 300 grms. phosphorus pentasulphide, 150 grms. broken glass, 300 grms. glacial acetic acid, and obtain 97 to 100 grms. of rectified thioacetic acid. This quantity, which does not require an hour to prepare, forms 300 c.c. of thioacetic solution, and suffices for more than 150 ordinary qualitative operations.

In the glass vessels there is left a hard black mass, which can be removed by heating with soda-lye. To save the trouble of cleansing, I use the well-known wine flasks common in Tuscany. These, without their straw cases, cost about 7 centimes; they are made of good thin green glass, and contain $2\frac{1}{2}$ to $2\frac{1}{4}$ litres. I cut off two-thirds of the neck, melt off the aperture, inserting it in an ascending T-tube. When the reaction is completed the flask is thrown away.

All the operation is performed under a good draught-wood with a large flame burning in order to burn all escaping gases of an evil odour.

This thioacetic method is, as it appears to me, important for the qualitative and quantitative recognition of arsenic in chemico-legal investigations. I have formerly mentioned that if a hydrochloric solution of arsenious or arsenic acid is boiled with thioacetate for about a minute, when the liquid is cold the arsenic is found to have been quantitatively precipitated from the clear liquid.

The difficulty of maintaining a long-continued current of hydrogen sulphide, absolutely free from arsenic—as required for judicial purposes—is well known. On the contrary, rectified thioacetic acid is always absolutely free from arsenic.—*Berichte*, xxviii., p. 1204.

QUANTITATIVE SEPARATIONS OF METALS IN ALKALINE SOLUTIONS BY HYDROGEN PEROXIDE.

By P. JANNASCH and E. v. CLOEDT.

SEPARATION OF BISMUTH, LEAD, AND MANGANESE FROM MERCURY.

1. Separation of Bismuth from Mercury.

As an initial point for their experiments the authors used pure metallic bismuth and mercuric oxide. The weighed quantities were heated in a covered porcelain capsule with 10 c.c. of concentrated nitric acid and 50 c.c. of water on the water-bath, until completely dissolved. The liquid is then slowly poured into a mixture of 25 to 30 c.c. of concentrated ammonia, 25 c.c. of hydrogen peroxide at 3 to 4 per cent, and 50 c.c. of water. There ensued a brisk effervescence of escaping oxygen, and the bismuth subsided as a yellowish-grey deposit of hydrated peroxide. It was then dissolved on the filter in dilute hot nitric acid, again precipitated as before, filtered, and weighed in a platinum crucible as bismuth peroxide.

Since for precipitating the bismuth we used hydrogen peroxide purified by distillation *in vacuo*, no correction for silica, alumina, &c., is needed. Still we must advise that the pure hydrogen peroxide should be used as fresh as possible, since its solutions on prolonged standing seem to attack sensitive kinds of glass, and may thus be anew contaminated with silica.

If the first deposit of bismuth is washed with extreme care, a single precipitation is sufficient for accurate separation. We have proved this in a couple of special experiments.

For the determination of the mercury the entire ammoniacal filtrate is evaporated down for the complete expulsion of the excess of ammonia, strongly acidified with sulphurous acid, the liquid poured into a larger beaker, diluted to at least 300 c.c., and lastly precipitated at a moderate heat with sulphuretted hydrogen. The further treatment of the mercury sulphide and its weighing are effected in the usual way.

2. Separation of Lead and Mercury.

The separation is effected by pouring the solution of the nitrate, acidified with nitric acid, into the ammoniacal oxidising liquid. The results are very satisfactory. It must be observed that, prior to filtration, the lead precipitate is allowed to stand for some time (thirty minutes to one hour), with occasional stirring, as otherwise traces of lead may remain in solution. The lead hydro-peroxide is filtered off, well washed with cold water, dissolved on the filter in dilute nitric acid (equal to about 10 c.c. of the concentrated acid), with a simultaneous addition of hydrogen peroxide, and precipitated again in the same manner.

3. Separation of Manganese and Mercury.

The separation of these metals is effected with great ease, which appears the more remarkable as manganese—in consequence of its tendency, when in the state of peroxide, to carry other oxides down with it—is apt to frustrate the smooth course of an analysis. The authors took, as their initial point, manganese-ammonium sulphate and mercuric oxide. From 0.3 to 0.4 grm. of each substance was dissolved in 50 c.c. water and 10 c.c. of concentrated nitric acid. This mixture is added to a liquid of 30 c.c. hydrogen peroxide, 30 c.c. strong ammonia, and 50 c.c. water. After heating for thirty minutes in a covered beaker on the water-bath, the precipitate is filtered and washed with a mixture of water, ammonia, and hydrogen peroxide, and finally with hot water. The precipitate may be ignited in a platinum or porcelain crucible, either whilst still moist or after a partial drying. The coarser particles are carefully crushed, and the ignition is continued until the weight becomes constant.—*Zeitschrift für Anorganische Chemie*.

ON THE ABSORPTION-SPECTRUM OF LIQUEFIED AIR.

By Professors LIVEING and DEWAR.

In a recent conversation on the absorption-spectrum of liquefied oxygen, M. Cornu suggested to us that it would be interesting to examine if the diffused absorption bands would develop as well when the density of oxygen is produced by a reduction of temperature at atmospheric pressure, as when the gas is compressed at higher temperatures.

M. Janssen has found that the intensity of these bands increases as the square of the density of oxygen, and has recently verified this result by observations of the solar spectrum in the desert of Sahara. This law, as we have already pointed out (*Proc. Roy. Soc.*, xlvii., p. 228), seems to indicate that these bands are due either to complex molecules produced by condensation, or to the encounters of molecules of an ordinary mass—encounters which are more frequent when their free path is diminished.

To reply to M. Cornu's question, we obtained liquefied air directly from the atmosphere by the cold due to the rapid evaporation of liquid oxygen under a low pressure. The method and the apparatus have been already described by Prof. Dewar (*Proc. Royal Institution*, xx., January, 1893).

The absorption due to liquefied air of the thickness of

1.9 c.m. was then compared directly with that of liquid oxygen, of the thickness of 0.4 c.m. The light which had traversed this latter medium was introduced, by means of a reflection-prism, into the field of vision of the spectro-scope at the same time as that which had traversed the liquid air. The position of the lamps was then regulated so that the brightness of the spectral regions free from bands was the same in the two spectra. Under these conditions it was observed that intensity of the absorption-bands was developed much more by 0.4 c.m. of liquid oxygen than by a depth of liquid air five times greater.

The vessels containing the liquids were open, the liquid air evaporated gradually, and as the boiling-point of nitrogen is below that of oxygen the nitrogen evaporated more rapidly, and the residual liquid contained a greater and greater proportion of oxygen. Therefore the absorption-bands become more and more intense, until they surpassed in intensity that of the slighter depth of oxygen.

Another portion of air liquefied like the former was rapidly mixed with an equal volume of liquid oxygen, and the absorption of this mixture was compared as above with that of liquid oxygen. We recognised that the absorption of 2.4 c.m. of the mixture was much greater than that of 0.4 c.m. of liquid oxygen. The density of the oxygen in this mixture was, in fact, three times greater than that of the oxygen in pure liquefied air, and, according to the law of Janssen, the absorption ought to become nine times greater. Our observations, therefore, agree with this result.

These observations agree also with the theory of the continuity of the liquid and the gaseous states. We must remember that air boils at a temperature lower than does oxygen, so that the two liquids to be compared were not at the same temperature by about 10°.

If the diffused absorption-bands of oxygen are produced by their mutual collisions in the gaseous and liquid states, it is permissible to suppose that they would be profoundly modified if the oxygen assumed the solid state. Hitherto oxygen has not yet been solidified in a state of purity, but liquid air is easily brought to the solid state by rapid evaporation under a low pressure (Dewar, *Proc. Royal Institution*, January 19, 1894).

Whether the solid thus obtained is homogeneous, or merely formed of a paste of solid nitrogen mixed with liquid oxygen, may be open to discussion, but in any case it is beyond doubt that the oxygen is at the lowest temperature which has been attained. Consequently, we have examined if a difference can be perceived between the absorptions of solid and of liquid air. There was no difference in the character of the absorptions, and very little in the intensities.

To gauge the effects of the temperature, we compared the absorption of a depth of 3 c.m. of liquid oxygen, boiling under a pressure of about 1 c.m., with that of an equal depth of the same liquid at the atmospheric pressure. With the coldest liquid, the bands in the orange and the yellow were appreciably elongated, enlarged especially on the more refrangible side. The weak band in the green was darker, and the band in the blue seemed also somewhat stronger. The difference of temperature might be about 17°, which does not seem much, though it is about the fifth part of the temperature of the warmer liquid.—*Comptes Rendus*, cxii., p. 162.

Examination of Seed-lac.—A. Gascard (*Journal de Pharmacie*).—Cold alcohol at 95 per cent extracts from the lac its most important resinous ingredient, which is important for the varnish manufacture, and is said to be a mixture of several acids of the fatty series, and to contain nitrogen. The portion soluble in boiling alcohol of the same strength separates out on cooling in the form of needles, and has the properties and composition of the waxes. It is a mixture of several esters of myricyl alcohol with more than 50 per cent of free myricyl alcohol.

ON THE SPECTRA OF ARGON.*

By WILLIAM CROOKES, F.R.S., &c.

THROUGH the kindness of Lord Rayleigh and Professor Ramsay I have been enabled to examine the spectrum of this gas in a very accurate spectroscopic, and also to take photographs of its spectra in a spectrograph fitted with a complete quartz train. The results are both interesting and important, and entirely corroborate the conclusions arrived at by the discoverers of argon.

The results of my examination are given in a table of wave-lengths, which follows, and on a map of the lines accurately drawn to scale, accompanying this paper. The map is 40 ft. long, and the probable error of position of any line on it is not greater than 1 m.m.

Argon resembles nitrogen in that it gives two distinct spectra, according to the strength of the induction current employed. But while the two spectra of nitrogen are different in character, one showing fluted bands and the other sharp lines, both the argon spectra consist of sharp lines. It is, however, very difficult to get argon so free from nitrogen that it will not show the nitrogen flutings superposed on its own special system of lines. I have used argon prepared by Lord Rayleigh, Professor Ramsay, and myself, and however free it was supposed to be from nitrogen, I could always at first detect the nitrogen bands in its spectrum. These, however, soon disappear when the induction spark is passed through the tube for some time, varying from a few minutes to a few hours. The vacuum tubes best adapted for showing the spectra are of the ordinary Plücker form, having a capillary tube in the middle. For photographing the higher rays which are cut off by glass I have used a similar tube, "end on," having a quartz window at one end. I have also used a Plücker tube made entirely of quartz worked before the oxy-hydrogen blowpipe. I have not yet succeeded in melting platinum or iridio-platinum wire terminals into the quartz, as they melt too easily, but a very good spectrum is obtained by coating the bulbs outside with tin-foil, connected with the terminals of the induction coil.

The pressure of argon giving the greatest luminosity and most brilliant spectrum is 3 m.m. At this point the colour of the discharge is an orange-red, and the spectrum is rich in red rays, two being especially prominent at wave-lengths 696.56 and 705.64. On passing the current the traces of nitrogen bands disappear, and the argon spectrum is seen in a state of purity. At this pressure the platinum from the poles spatters over the glass of the bulbs owing to what I have called "electrical evaporation,"† and I think the residual nitrogen is occluded by the finely-divided metal. Similar occlusions are frequently noticed by those who work much with vacuum tubes.

If the pressure is further reduced, and a Leyden jar intercalated in the circuit, the colour of the luminous discharge changes from red to a rich steel blue, and the spectrum shows an almost entirely different set of lines. The two spectra, called for brevity red and blue, are shown on the large map, the upper spectrum being that of "blue" argon, and the lower one that of "red" argon. It is not easy to obtain the blue colour and spectrum entirely free from the red. The red is easily got by using a large coil‡ actuated with a current of 3 amperes and 6 volts. There is then no tendency for it to turn blue.

The blue colour may be obtained with the same coil by actuating it with a current of 3.84 amperes and 11 volts, intercalating a jar of 50 square inches surface. The make-and-break must be screwed up so as to vibrate as rapidly as possible. With the small coil a very good blue

colour can be obtained by using three Grove cells and a Leyden jar of 120 square inches surface, and a very rapid make-and-break. It appears that an electromotive force of 27,600 volts is required to bring out the red, and a higher E.M.F. and a very hot spark for the blue. It is possible so to adjust the pressure of gas in the tube that a very slight alteration of the strength of the current will cause the colour to change from red to blue, and *vice versa*. I have occasionally had an argon tube in so sensitive a state that with the commutator turned one way the colour was red, and the other way blue. Induction coils actuated by a continuous current are never symmetrical as regards the polarity of the induced current, and any little irregularity in the metallic terminals of the vacuum tube also acts as a valve. The red glow is produced by the positive spark, and the blue by the negative spark.

I have taken photographs of the two spectra of argon partly superposed. In this way their dissimilarity is readily seen.* In the spectrum of the blue glow I have counted 119 lines, and in that of the red glow 80 lines, making 199 in all; of these, 26 appear to be common to both spectra.

I have said that the residual nitrogen is removed by sparking the tube for some time when platinum terminals are sealed in. This is not the only way of purifying the argon. By the kindness of Professor Ramsay I was allowed to take some vacuum tubes to his laboratory and there exhaust and fill them with some of his purest argon. On this occasion I simultaneously filled, exhausted, and sealed off two Plücker tubes, one having platinum and the other aluminium terminals. On testing the gas immediately after they were sealed off, each tube showed the argon spectrum, contaminated by a trace of nitrogen bands. The next day the tube with platinum terminals was unchanged, but that having aluminium terminals showed the pure spectrum of argon, the faint nitrogen bands having entirely disappeared during the night. After an hour's current and a few days' rest the tube with platinum terminals likewise gave a pure argon spectrum. When a mixture of argon with a very little nitrogen is submitted to the induced current in a tube made of fused and blown quartz, without inside metallic terminals, the nitrogen bands do not disappear from the argon spectrum, but the spectra of argon and nitrogen continue to be seen simultaneously.

A vacuum tube was filled with argon and kept on the pump while observations were made on the spectrum of the gas as exhaustion proceeded. The large coil was used with a current of 8.84 amperes and 11 volts; no jar being interposed. At a pressure of 3 m.m. the spectrum was that of the pure red glow. This persisted as the exhaustion rose, until at a pressure of about half a m.m. flashes of blue light made their appearance. At a quarter of a m.m. the colour of the ignited gas was pure blue, and the spectrum showed no trace of the red glow.

A striking instance of a change of spectrum from nitrogen to argon was shown in a tube filled with argon kindly sent me by Lord Rayleigh. It had been prepared from the atmosphere by sparking, and it was considered to contain about 3 per cent of nitrogen. This argon was passed into an exhausted tube and then rarefied to a pressure of 75 m.m. and kept on the pump. At this pressure the nitrogen conducted all the induction current, the spectrum showing nothing but the nitrogen bands. The pump was slowly kept going, and spectrum observations were continuously taken. When the pressure fell to about 3 m.m. a change came over the spectrum, the nitrogen bands disappeared, and the spectrum of argon took its place; the only contamination being a little aqueous vapour, due to my not having sufficiently dried the gas. I took photographs of the spectrum given by this tube in the two stages, one show-

* From the *Philosophical Transactions of the Royal Society*, vol. clxxvi. (1895), A., pp. 243-251.

† *Roy. Soc. Proc.*, vol. I, p. 88, June, 1891.

‡ The coil used has about sixty miles of secondary wire, and when fully charged gives a torrent of sparks 24 inches long. The smaller coil gives six-inch sparks when worked with six half-pint Grove cells.

* Photographs of the different spectra of argon, and other gaseous spectra for comparison, were projected on the screen.

ing the pure nitrogen bands and the other the argon lines, each being compared with the spectrum of argon prepared by Professor Ramsay. Observations have shown that the spectra given by argon, obtained by the sparking method of Lord Rayleigh and by the magnesium method of Prof. Ramsay from the atmosphere, are identical.

It was of interest to see how little argon could be detected in admixture with nitrogen by combined pumping and passage of the current. Some argon prepared by myself,* having 60 to 70 per cent of nitrogen with it, was put into a small tube furnished with large platinum terminals. Exhaustion was carried to 3 m.m., and the tube was then sealed off. The spark from the large coil actuated with a current of 3·84 ampères and 11 volts was then put on, and the spectrum examined continuously. At first it showed only the nitrogen bands. In about half an hour the nitrogen began to fade and the argon lines appear, and in a few minutes later the tube was just short of non-conducting, the colour of the gas was rich steel-blue, and the spectrum was that of the blue argon glow. Here the small diameter of the bulbs of the tube and the large platinum wires facilitated much spattering or "electrical evaporation" of the platinum. The pressure also was the one most suitable for that phenomenon. To this I attribute the rapid occlusion of the residual nitrogen.

An experiment was now made to see if the small quantity of argon normally present in the atmosphere could be detected without previous concentration. Nitrogen was prepared from the atmosphere by burning phosphorus, and was purified in the usual manner. This gas, well dried over phosphoric anhydride, was passed into a vacuum tube, the air washed out by two fillings and exhaustions, and the tube was finally sealed off at a pressure of 52 m.m. It was used for photographing the band spectrum of nitrogen on several occasions, and altogether it was exposed to the induction current from the large coil for eight hours before any change was noticed. The last time I used it for photographing the nitrogen spectrum difficulty was experienced in getting the spark to pass, so I increased the current and intercalated a small jar. The colour immediately changed from the reddish yellow of nitrogen to the blue of argon, and on applying the spectroscope the lines of argon shone out with scarcely any admixture of nitrogen bands. With great difficulty and by employing a very small jar I was able to take one photograph of this changed spectrum and compare it with the spectrum of argon from Professor Ramsay, both being taken on the same plate, but the tube soon became non-conducting, and I could not then force a spark through, except by employing a dangerously large current. Whenever a flash passed it was of a deep blue colour. Assuming that the atmosphere contains 1 per cent of argon, the 3 m.m. of nitrogen originally in the tube would contain 0·03 m.m. of argon. After the nitrogen had been occluded by the spattered platinum, this pressure of argon would be near the point of non-conduction.

In all cases when argon has been obtained in this manner the spectrum has been that of the blue-glowing gas. Very little of the red rays can be seen. The change from red to blue is chiefly dependent on the strength and heat of the spark: partly also on the degree of exhaustion. Nitrogen, when present, conducts the current easiest. As the exhaustion increases and the conductivity of the nitrogen diminishes, that of the red-glowing argon rises, until at a pressure of about 3 m.m. its conductivity is at the greatest and the luminosity is best. Beyond that point the conductivity of the red form seems to get less, and that of

the blue form to increase, till the vacuum approaches a fraction of a m.m., when further pumping soon renders it non-conducting. It is not improbable, and I understand that independent observations have already led both the discoverers to the same conclusion—that the gas argon is not a simple body, but is a mixture of at least two elements, one of which glows red and the other blue, each having its distinctive spectrum. The theory that it is a simple body has, however, support from the analogy of other gases. Thus, nitrogen has two distinct spectra, one or the other being produced by varying the pressure and intensity of the spark. I have made vacuum tubes containing rarefied nitrogen which show either the fluted band or the sharp line spectrum by simply turning the screw of the make-and-break: exactly as the two spectra of argon can be changed from one to the other.

The disappearance of the red glow and the appearance of the blue glow in argon as the exhaustion increases also resembles the disappearance of the red line of hydrogen when exhaustion is raised to a high point. Plücker, who was the first to observe this occurrence, says: "When Ruhmkorff's small induction coil was discharged through a spectral tube enclosing hydrogen, which was gradually rarefied to the highest tenuity to be reached by means of Geissler's exhaustor, finally the beautiful red colour of the ignited gas became fainter, and passed gradually into an undetermined violet. When analysed by the prism, H_{α} (the red, C, line) disappeared, while H_{β} (the green, F, line), though fainter, remained well defined. Accordingly, light of a greater length of wave was the first extinguished."

The line spectrum of nitrogen is not nearly so striking in brilliancy, number, or sharpness of lines as are those of argon, and careful scrutiny fails to show more than one or two apparent coincidences between lines in the two spectra. Between the spectra of argon and the band spectrum of nitrogen there are two or three close approximations of lines, but a projection on the screen of a magnified image of the two spectra partly superposed shows that two at least of these are not real coincidences.

I have looked for indications of lines in the argon spectra corresponding to the corona line at 531·7, the aurora line at 557·1, and the helium line at 587·5, but have failed to detect any line of argon sufficiently near these positions to fall within the limits of experimental error.

I have found no other spectrum-giving gas or vapour yield spectra at all like those of argon, and the apparent coincidences in some of the lines, which, on one or two occasions are noticed, have been very few, and would probably disappear on using a higher dispersion. Having once obtained a tube of argon giving the pure spectra, I can make no alteration in it except that which takes place on varying the spark or increasing the exhaustion, when the two spectra change from one to the other. As far, therefore, as spectrum work can decide, the verdict must be that Lord Rayleigh and Professor Ramsay have added one, if not two, members to the family of elementary bodies.

BLU.		RED.	
Wave-length.	Intensity.	Wave-length.	Intensity.
		764·6	2
		750·6	4
		737·7	3
		726·3	2
		705·64	10
		696·56	9
		684·2	2
		675·4	6
		666·4	6

* When a current of 65 volts and 15 ampères alternating 130 times a second is passed through the primary of my large coil, an arching flame, consisting of burning nitrogen, issues from each of the secondary poles, meeting in the middle. When once started the poles can be drawn asunder, till the flame bridges across 212 m.m. When the terminals are more than 46 m.m. apart the flame will not strike across. By enclosing this flame in a reservoir over alkaline water, and feeding it with air and oxygen, I can burn up a litre of air an hour.

* "On the Spectra of Ignited Gases and Vapours," by Drs. Plücker and Hittorf, *Phil. Trans.*, Part 1, clv., p. 21.

BLU.		RAD.				BLU.		RAD.			
Wave-length.	Intensity.	Wave-length.	Intensity.			Wave-length.	Intensity.	Wave-length.	Intensity.		
662.8	4					426.60	6	426.60	4	Coincident.	
		640.7	9			425.95	8	425.95	9	Coincident.	
		637.7	2			425.15	2	425.15	3	Coincident.	
		630.2	4			422.85	6				
		628.1	2			420.10	10	420.10	10	Coincident.	
623.2	4					419.80	9	419.80	9	Coincident.	
		621.0	6			419.15	9	419.15	9	Coincident.	
617.3	6	617.3	6	Coincident.		418.30	8	418.30	8	Coincident.	
		614.3	2			416.45	8	416.45	4	Coincident.	
612.0	6					415.95	10	415.95	10	Coincident.	
		609.9	4					415.65	6		
		605.6	2			413.15	3				
		604.5	3			410.50	8				
603.8	8	603.8	8	Coincident.		407.25	8				
		593.5	1			404.40	8	404.40	9	Coincident.	
592.6	4	592.6	4	Coincident.		403.30	1				
		590.9	6			401.30	8				
		588.7	6			397.85	1				
		585.8	4			396.78	3				
		583.4	2			394.85	9	394.85	10	Coincident.	
		580.3	1			394.35	3				
		577.1	2			393.18	3				
		574.6	6			392.85	9				
		568.3	2			392.75	3				
		565.1	9			391.50	1				
		561.0	9					390.45	8		
		556.7	2			389.20	5				
		555.7	10			387.55	2				
		552.0	1			387.18	2				
		550.1	2			386.85	8				
		549.65	8			385.15	10				
		545.6	6			384.55	1				
		544.4	2			383.55	2	383.55	3	Coincident.	
		542.1	4			382.75	2				
		525.8	6			380.95	4				
		522.2	7			380.35	1				
		518.58	10			379.95	1				
		516.5	9			378.08	9				
514.0	10							377.15	1		
506.5	10	506.5	4	Coincident.		377.05	2				
501.2	2	501.2	4	Coincident.		376.60	8				
500.7	9					373.85	3				
496.55	9	496.55	4	Coincident.		372.98	10				
493.8	10	493.8	2	Coincident.		371.80	4				
487.9	10	487.9	4	Coincident.				363.25	2		
484.75	1					363.17	1				
480.50	7							362.37	1		
476.30	1							362.28	1		
473.45	6					361.75	2				
472.66	2					360.50	3	360.50	5	Coincident.	
		470.12	8			358.70	10				
465.65	5					358.03	9				
		462.95	5			357.50	9				
460.80	8					356.65	2	356.65	4	Coincident.	
		459.45	2			356.40	2				
458.69	6							356.28	1		
457.95	6					356.00	2				
454.35	7					355.82	7				
		451.40	2			355.45	4	355.45	6	Coincident.	
450.95	8	450.95	9	Coincident.		354.75	4				
447.83	6					354.45	7				
442.65	10					353.43	4				
442.25	10					352.05	3				
439.95	10					351.92	4				
437.65	9					351.35	6				
436.90	9					350.88	4				
434.85	10					349.00	10				
		434.50	5			347.57	7				
433.35	9	433.35	9	Coincident.		345.35	1				
		430.05	9			338.80	1				
429.90	9					309.27	5				
427.70	3					308.48	4				
427.20	7	427.20	8	Coincident.		306.47	2				

BLUE.	
Wave-length.	Intensity.
304.27	3
299.82	1
297.86	1
294.27	2
292.96	1
283.02	1
279.44	2
273.45	2
270.72	0.5
269.30	1
266.12	2
265.26	3
262.95	1
257.12	2
256.07	1
248.49	1
243.85	2
224.66	3

119 lines in the "Blue" spectrum.
80 lines in the "Red" spectrum.

199 total lines.
26 lines common to the two spectra.

CHROMATES OF THE RARE EARTHS: CHROMATES OF THORIUM.

By CHASE PALMER.

BELIEVING that a study of the action of an acid of feeble energy upon the weak bases of the tin group—or Fourth Group of Mendeleeff's Periodic System—would throw new light upon this interesting family of elements, I have undertaken a comparative study of the action of chromic acid upon the oxides of the rarer metals of this group, and of the conduct of their salts towards the alkaline chromates.

The chromates of the rare elements of this group have hitherto received but little attention from chemists. The earliest allusion to a chromate of a rare earth was made in 1863 by J. J. Chydenius ("Thorerde und deren Verbindungen," *Ann. der Phys. Pogg.*, cxix., 43). This author observes that thorium hydroxide is soluble in chromic acid. He states that from the resulting solution, evaporated over sulphuric acid, he obtained normal thorium chromate as a soluble salt containing eight molecules of water of crystallisation. Chydenius further states that potassium dichromate produces no precipitate when added to a solution of thorium chloride, until after the mixture is neutralised with ammonia, whereby a basic salt of thorium is thrown down. The only other allusion to a chromate of a rare metal of the Fourth group, in the literature accessible to me, is made by Pattison and Clarke (*CHEM. NEWS*, xvi., 259). These chemists observed that by heating the residue from an evaporated solution of the hydroxides of cerium, lanthanum, and didymium in chromic acid, the cerium compound was rendered insoluble; but there is no evidence that they determined the composition of the insoluble product.

Thorium was chosen as the first element for the present research on account of the highly developed basic properties of its oxide. Contrary to the observations of Chydenius, I have found, not only that a difficultly soluble salt, having the composition of normal thorium chromate, separates spontaneously from a solution of thorium hydroxide in chromic acid, but also that the same compound is precipitated by potassium dichromate from thorium nitrate without the aid of a neutralising alkali. I have also found that potassium chromate produces the same compound indirectly from a soluble thorium salt.

Thorium Hydroxide and Chromic Acid.—Pure freshly

precipitated thorium hydroxide] was added in portions to a solution of pure chromium trioxide in water. The quantity of the trioxide was slightly in excess of the amount required to form the normal chromate. The hydroxide was quickly dissolved at first, but afterwards the acid attacked it more sluggishly. A flocculent orange precipitate soon appeared, and finally settled as a fine powder. Under the microscope this product shows a crystalline structure. The formation of the orange precipitate takes place more quickly at 90° C. than at the ordinary temperature.

Dried at 120° C. to constant weight the product was analysed:—

0.2016 grm. substance at 180° lost 0.0072 grm. H₂O and gave 0.1114 grm. ThO₂ and 0.0626 grm. Cr₂O₃.

Calculated for Th(CrO ₄) ₂ ·H ₂ O.		Found.
H ₂ O		3.73
Th		48.05
Cr		21.71

Thorium Chromate from Chromic Acid Solution.—Pure freshly-precipitated thorium hydroxide, in small portions at a time, was stirred in a cold solution of chromic acid as long as it was taken up. At the first appearance of the orange precipitate, the latter was filtered off, and the solution evaporated over sulphuric acid *in vacuo*. From the concentrated solution thorium chromate separated out in orange-coloured scales containing two molecules of water of crystallisation and one molecule of water of constitution.

Dried to constant weight over sulphuric acid the salt was analysed.

I. 0.215 grm. substance lost 0.0148 grm. H₂O at 120°; at 180° it lost 0.007 grm. H₂O additional, and gave 0.1104 grm. ThO₂ and 0.0631 grm. Cr₂O₃.

II. 0.2155 grm. substance lost 0.015 grm. H₂O at 120°; at 180° it lost 0.0068 grm. H₂O additional, and gave 0.111 grm. ThO₂ and 0.0622 grm. Cr₂O₃.

Calculated for Th(CrO ₄) ₂ ·3H ₂ O.		Found.	
		I.	II.
2H ₂ O		6.90	6.96
H ₂ O		3.46	3.25
Th		44.71	45.12
Cr		20.20	20.12

Thorium Nitrate and Potassium Dichromate.—On mixing the boiling solutions of these salts in the proportion of one molecule of the nitrate to two molecules of the dichromate, hydrated thorium chromate was precipitated at once as a fine orange powder. In this way 78 per cent of the theoretical yield was obtained.

0.1986 grm. substance, dried at 120°, lost 0.0073 grm. H₂O at 180° and gave 0.1095 grm. ThO₂ and 0.0668 grm. Cr₂O₃.

		Found.
H ₂ O		3.67
Th		48.35
Cr		21.34

When the cold solutions of thorium nitrate and potassium dichromate were mixed no immediate precipitation occurred, but in a short time a precipitate began to form. After standing twenty-four hours the orange precipitate that had formed meanwhile was filtered off, washed, and dried at 120°.

0.1817 grm. substance lost 0.0064 grm. H₂O at 180°, and gave 0.1008 grm. ThO₂ and 0.0569 grm. Cr₂O₃.

		Found.
H ₂ O		3.52
Th		48.75
Cr		21.47

The filtrate from this precipitate was heated to 90°. At 60° a second precipitation of the thorium chromate

occurred. The first yield was 65 per cent, and 14 per cent additional was obtained by heating the filtrate. The total yield (79 per cent) closely corresponds with the yield obtained by precipitating the compound at once from a boiling solution.

The mother-liquor from the second precipitate was reduced to small volume, but no further precipitation occurred. By evaporating it to dryness a very soluble crystalline product was left, but it could not be isolated for examination.

Thorium Nitrate and Potassium Chromate.—There are two stages in the formation of hydrated thorium chromate from thorium nitrate and potassium chromate. When a solution of thorium nitrate is treated with a solution of potassium chromate (one molecule of the former to three molecules of the latter), the precipitate, which at once forms, dissolves immediately until the mixture is complete. Then a dense golden yellow precipitate separates from the solution. The liquid meanwhile becomes red, owing to the formation of potassium dichromate. By promptly removing the yellow precipitate from contact with the fluid it was found, on analysis, to be basic thorium chromate.

0.2367 grm. substance dried at 100° gave 0.1635 grm. ThO_2 and 0.0459 grm. Cr_2O_3 .

	Calculated for $\text{Th}(\text{OH})_2\text{CrO}_4$.	Found.
Th	60.66	60.70
Cr	13.70	13.29

If the basic thorium chromate be allowed to remain in contact with the supernatant liquid, it is gradually changed into the orange precipitate, which, upon analysis, proved itself to be the same hydrated thorium chromate already described. During this transformation the red liquid is changed to the bright yellow colour of potassium chromate.

Analysis of the final product dried at 120°:—
0.2136 grm. substance at 180° lost 0.0081 grm. H_2O and gave 0.1175 grm. ThO_2 and 0.0678 grm. Cr_2O_3 .

	Found.
H_2O	3.79
Th	48.34
Cr	21.77

The complete reaction may be expressed by the two equations:—

1. $\text{Th}(\text{NO}_3)_4 + 3\text{K}_2\text{CrO}_4 + \text{H}_2\text{O} = \text{Th}(\text{OH})_2\text{CrO}_4 + \text{K}_2\text{Cr}_2\text{O}_7 + 4\text{KNO}_3$.
2. $\text{Th}(\text{OH})_2\text{CrO}_4 + \text{K}_2\text{Cr}_2\text{O}_7 = \text{Th}(\text{CrO}_4)_2 \cdot \text{H}_2\text{O} + \text{K}_2\text{CrO}_4$.

The hydrated thorium chromate always has a full orange colour, which it does not lose even after prolonged heating at 130°. The colour of the anhydrous salt is ochreous yellow. At 22°, 1 part of the salt is soluble in 284 parts of water. It is readily soluble in hydrochloric acid and in ammonium carbonate. At a dull red heat it is decomposed into thorium dioxide and chromic oxide. Heated in a platinum crucible over a Bunsen lamp the substance lost 10.41 per cent in weight. For the loss of three oxygen atoms to form ThO_2 and Cr_2O_3 the required loss in weight is 10.32 per cent.

Constitution of the Orange Chromate—It is noteworthy that the orange chromate of thorium always contains one molecule of firmly bound water, whether the substance be formed by slow crystallisation from a chromic acid solution, or by precipitation from a soluble salt, or formed from the insoluble basic chromate. The substance may be regarded simply as hydrated normal thorium chromate, $\text{Th}(\text{CrO}_4)_2 \cdot \text{H}_2\text{O}$, or it may be a basic dichromate of thorium having the constitution expressed by the formula



Before expressing an opinion as to the more probable constitution of the orange chromate, I shall attempt to

gather more knowledge of these chromates and of the compounds of chromic acid with the related elements.

Zirconium hydroxide is attacked by chromic acid less readily than is thorium hydroxide. It can be completely dissolved in an excess of the acid. A yellow precipitate was obtained by boiling this solution. From an analysis, the product appears to be a basic salt.

A similar yellow precipitate is obtained by the action of potassium dichromate on zirconium chloride. The precipitate, dried over sulphuric acid, gave 41.24 per cent Zr and 16.38 per cent Cr. It is probably a basic salt.

I intend to make a thorough study of the chromates of zirconium and of the other elements of the Fourth Group.

I wish to express here my hearty thanks to Professor Edgar F. Smith, through whose generous hospitality I have enjoyed the facilities of the John Harrison Chemical Laboratory of the University of Pennsylvania, where the work described in this paper has been done.—*American Chemical Journal*, xvii., No. 5.

THE WET ASSAY FOR COPPER.

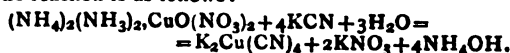
By R. S. DULIN.

It seems difficult for the metallurgical chemists of this country to settle upon a uniform method for the rapid determination of copper. We should have a standard method, applicable for all commercial work, which would be fairly accurate under as many possible varying conditions, so that results obtained from the same ore, by different chemists, should be substantially uniform. For about nine months past I have been engaged upon an extended series of experiments, having for their object a determination of the chief causes for variation and error in the methods most generally employed, and for the purpose of finding a modification of common methods which would be an improvement upon those now used. At the same time I have made myself conversant with much of the current literature upon the subject, and the observations herein offered, while based upon my individual experiments, are corroborated, in most part, by the published results of others.

There are at present three well-recognised methods employed in the United States for the determination of copper. Each method has its own advocates, and it is perfectly fair to say that either method, in the hands of a skilled chemist, thoroughly understanding the reactions of the methods, working with all due care, will yield substantially the same results. The methods referred to are:—

1. The cyanide method. 2. The iodide. 3. The electrolytic. A colorimetric method is also employed for the determination of copper when the percentages fall below 2 per cent. I have made no particular study of this method, and, as it is only employed in special cases, I shall make no further reference to it.

The cyanide method depends upon the fact that, when a solution of potassium cyanide is run into an ammoniacal solution of copper, the blue colour is discharged. The reaction is as follows:—



This method is fully described in Furman's "Manual of Practical Assaying." The following precautions should always be carefully observed:—1. The bulk of the liquid titrated should always be uniform; by inattention to this an error of from 2 to 3 per cent is possible. 2. The solution should always be cooled to the temperature of the laboratory before titrating, otherwise an error of about 3 per cent is possible. 3. The amount of ammonia added should be nearly constant, otherwise the possible error may amount to as much as 5 per cent, or even more.

These precautions are general, and must always be carefully observed in every modification which may be made in the method. In the ordinary modification of the method, ferric hydroxide is almost certain to be precipitated upon the addition of the ammonium hydroxide. If the amount be small, no error is apt to occur, but it should always be filtered off. If the amount be large, it is not easy to wash out all of the copper salt, thereby causing lower results, unless large quantities of wash-water are employed, thus increasing and varying the bulk. The error arising from increased bulk may be obviated, by taking, after mixing, an aliquot part of the solution; if the solution be not thereby made very dilute the error is so slight that it may be neglected. If salts of manganese are present the end reaction cannot be determined, owing to the liquid first turning green, finally black. The presence of large quantities of calcium, I found, confused the end reaction, causing error of importance. Experiments made showed that magnesia did not interfere, and the presence of antimony and arsenic was found to cause no sensible variations.

Zinc, which is almost certain to be present in varying amount, is a possible source of great error. The following results were obtained from a large number of carefully conducted experiments. Only the averages are given, and they are substantially the same as the extremes. In these experiments the bulk of the liquid varied from 25 to as much as 50 c.c., thereby causing a slight error, for which no correction has been made. This error would not substantially change the results. Careful attention was paid to the precautions previously enumerated.

Weight of copper.	Weight of zinc.	Cyanide used.	Increase.
0.05	0.00	10.4 c.c.	—
0.05	0.01	11.0 "	0.6 c.c.
0.05	0.02	11.7 "	1.3 "
0.05	0.03	12.3 "	1.9 "
0.05	0.04	12.9 "	2.5 "
0.05	0.05	14.0 "	3.6 "
0.05	0.06	16.1 "	5.7 "
0.05	0.07	18.9 "	8.5 "
0.05	0.08	21.6 "	11.2 "
0.05	0.09	24.3 "	13.9 "

These results show that there is a gradual increase of about six-tenths c.c. in the amount of the cyanide solution required, until the amount of zinc present nearly equals the amount of copper, when the increase becomes variable, until the amount of zinc becomes greater than the amount of copper to the extent of 20 per cent, when the increase, though larger, about 2½ c.c., again becomes regular.

The effects of cadmium are similar, as shown by the following results, which are also the averages of a large number of experiments, in which the extremes are farther removed from the mean than was found with zinc. As in the preceding experiments, the precautions previously enumerated were very carefully observed, except in the case of bulk, in which the variations were identically the same as with the experiments with zinc.

Weight of copper.	Weight of cadmium.	Cyanide used.	Increase.
0.05	0.00	10.4 c.c.	—
0.05	0.01	10.6 "	0.2 c.c.
0.05	0.02	10.8 "	0.4 "
0.05	0.03	11.1 "	0.7 "
0.05	0.04	11.6 "	1.2 "
0.05	0.05	12.0 "	1.6 "
0.05	0.06	12.4 "	2.0 "
0.05	0.07	13.5 "	3.1 "
0.05	0.08	14.5 "	4.1 "

These results show that there is a gradually accumulating increase in the consumption of cyanide due to the presence of cadmium. As cadmium is a constituent

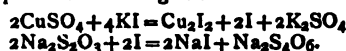
usually found associated with copper, it must be removed if reliable results be required. Silver also interferes, but in a regular way. If the amount of silver be known, by previous assay, it is best allowed for by calculation.

The following modification of the cyanide method has been thoroughly tested, under the immediate supervision of Prof. Seamon, and it is recommended as giving results equal in value to those obtained by the electrolytic method.

The ore is treated according to the method described on page 161 of Furman's "Manual of Assaying." In this way a solution of the copper salt is obtained, practically free from lead and silver. This solution is boiled with strips of aluminum foil, resulting in the complete precipitation of the copper together with any silver which may remain in the solution, which is always so small as to be negligible, as I have demonstrated by a number of experiments upon different ores. If cadmium be present it is only partially precipitated, beginning after the copper is thrown down. If care be taken to stop the boiling, immediately after the copper is precipitated, which can be determined with constant practice by the eye, the amount of cadmium precipitated is so small as not to cause sensible error. The liquid is decanted from off the aluminum foil and copper, quickly washed several times with hot water, care being taken not to wash away any particles of the copper; 3 c.c. of nitric acid are then added to the flask, and boiled to dissolve the copper; the solution is then treated with ammonium hydroxide as in the usual way, and titration is made with the usual solution of cyanide.

This method has been very carefully tested, and the results were so satisfactory, and nearly uniform, that I recommend it as being as accurate as the electrolytic method, under the conditions in which the latter is usually employed.

The iodide method is most commonly employed in the Lake Superior District and in foreign countries, where it is regarded with much favour. Many chemists regard it as more accurate than the cyanide or electrolytic methods, and there is no doubt from my experiments that it is more accurate than the ordinary modification of the cyanide and equal to that of the electrolytic. The method depends upon the following reactions:—



The best results are obtained when the copper is precipitated with aluminum foil, as previously described under the cyanide method. The method is fully described in Furman's "Manual of Assaying," and I only desire to call attention to the necessity for attending to the following precautions:—

1. The presence of iron in about equal amounts with the copper requires more "hypo," increasing the amount of copper to the extent of 2 to 3 per cent. 2. The solution should be titrated cold. 3. The presence of large amounts of alkaline salts, particularly sodium sulphate, decreases the amount of copper. 4. The presence of bismuth clouds the end reactions. My experience with the modification of this method, in which the copper is first precipitated with aluminum foil, convinces me that with this change the results are as accurate as those obtained with the modified cyanide method; but it is not so rapid, owing to the time lost at various stages: this is an important factor in the adoption of any method for metallurgical work, when thirty and forty assays must be completed every day. The method is a little more difficult to manipulate than the cyanide method.

The electrolytic method is perhaps the most highly favoured in this country. It has the reputation for greatest accuracy. It requires more time than either of the other; but since it is easy to regulate the work, so that the battery will precipitate during the night, this is not of so much importance. In regular routine work, after solution is effected, the copper should be precipitated with hydro-

gen sulphide, otherwise many interfering metals are apt to be present and deposited with the copper. I have found that errors from this source are largely, if not entirely, eliminated, if deposition be made from a solution containing a large amount of nitric acid. My best results were obtained when I added 20 c.c. of strong nitric to about 150 c.c. of solution. This holds up the other metals, but a stronger current is required to precipitate all of the copper, and more attention must be paid to proper and rapid manipulation after precipitation. This method is much improved by previously precipitating the copper from its solution by boiling with aluminum foil and then re-dissolving the copper in nitric acid. The following results, obtained from the same sample, carefully prepared, obtained by the three methods, furnish a fair idea of the relative values of the several methods.

A copper matte, containing 20.15 per cent of copper, as determined by a large number of analyses, made by several different assayers and by different methods, was run by each method. The amount of copper in the second matte, determined from the same data, was found to be 28 per cent, while the per cent of copper in the ore was 30.18.

The results obtained by the cyanide method were respectively 20.15, 27.95, and 30.20 per cent. The copper was first precipitated with the aluminum foil. The same substances, with the iodide method, first precipitating with aluminum foil, gave, respectively, 20.25, 28.35, and 30.3 per cent. By the electrolytic method the same substances gave, respectively, 20.045, 28.15, and 30.05 per cent.

These results justify the statement that the iodide method, with the aluminum modification, gives results usually one-tenth to three-tenths per cent too high, while the electrolytic method is too high or too low, according to the amount of metallic substances present precipitable by the electric current; and the cyanide method gives results which are practically correct.—*Journal of the American Chemical Society*, xvii., p. 346.

A REVISION OF THE ATOMIC WEIGHT OF STRONTIUM.

FIRST PAPER: THE ANALYSIS OF STRONTIC BROMIDE.*

By THEODORE WILLIAM RICHARDS.

(Concluded from p. 56).

Ratio of Argentite to Strontic Bromide.

In many of the preceding determinations the bromide of silver resulting from the decomposition was weighed.

Ratio of Strontic and Argentite Bromides.

No. of Anal.	No. of Spec.	First Series.		Ratio SrBr ₂ 2AgBr	At. wt. of Strontium.
		Weight of Strontic Bromide taken. Gms.	Weight of fused Argentite Bromide found. Gms.		
13.	I.	1.6086	2.4415	65.886	87.669
14.	II.	1.8817	2.8561	65.884	87.662
15.	III.	4.5681	6.9337	65.883	87.657
		8.0584	12.2313	65.8834	87.660
		Second Series.			
16.	III.	1.49962	2.27625	65.881	87.652
17.	III.	2.41225	3.66140	65.883	87.660
18.	III.	2.56153	3.88776	65.887	87.674
19.	V.	6.15663	9.34497	65.882	87.654
		12.63003	19.17038	65.883	87.659

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy*.

In every case a slight excess of silver nitrate was added, to render the argentic bromide wholly insoluble in the filtrate. The very slight amount which may have been dissolved by the wash water during its brief contact with the precipitate was not considered. The precipitate was collected upon a Gooch crucible; and the traces (0.04 to 0.2 m.grm.) of asbestos carried through were collected upon a small washed filter, ignited separately, weighed, and added to the gain in weight of the crucible. From this was subtracted the loss in weight of the precipitate upon fusion in a covered porcelain crucible. A description of the dark room used for the experiments, and many other precautions and details, will be found in other papers (*Proc. Amer. Acad.*, xxviii., 24; xxxix., 74). The results are tabulated below.

It remains only to bring together the results into one table.

Final Averages.

Oxygen = 16.000.

			Strontium equals
I.	2Ag : SrBr ₂	First Series	87.644
II.	" "	Second Series	87.663
III.	" "	Third Series	87.668
IV.	2AgBr : SrBr ₂	First Series	87.660
V.	" "	Second Series	87.659

Total average = 87.659

Average, rejecting I. above = 87.663

The last average is probably most nearly correct.

The analysis of strontic chloride has already been begun, and the preliminary results indicate that the results given above are certainly not too high. For the present, then, the atomic weight of strontium may be taken as 87.66 if oxygen is 16.00, 87.44 if oxygen is 15.96, and 87.01 if oxygen is 15.88.

NOTICES OF BOOKS.

A Text-Book of the Science and Art of Bread-Making, including the Chemistry and Analytical and Practical Testing of Wheat, Flour, and other Materials used in Baking. By WILLIAM JAGO, F.I.C., F.C.S., Chemist to the National Association of Master Bakers and Confectioners of Great Britain and Ireland; Honorary Consultative Examiner in Bread-Making to the City and Guilds of London Institute for the Advancement of Technical Education; Cantor Lecturer on "Modern Developments of Bread-Making" to the Society of Arts, London, &c. London: Simpkin, Marshall, Hamilton, Kent, and Co., Ltd. 1895. 8vo., pp. 648.

THE baker holds a position essentially distinct from that, e.g., of the grocer, draper, &c. He does not merely buy in the wholesale market and sell by retail; he obtains raw material and supplies it to his customers after it has undergone changes necessary to its general use as food. Hence he has not merely to make a judicious selection of raw materials, but to carry out the changes involved in the conversion of flour into bread.

To effect these changes successfully and economically he must have acquaintances with certain principles, mainly chemical, micro-biological, and physical. Without such knowledge he may certainly, by rule-of-thumb, turn out good bread from January to December; but he is at the mercy of accidents. An unusual sample of flour or of yeast may any day show him to his cost that he is not master of the situation.

The adulteration of flour is judiciously dealt with; but we see here nothing to shake our belief that the intentional sophistication of flour and breads is less prevalent than it was formerly.

The remarks on aluminous baking-powders (p. 489) convince us that, as long as our Courts tolerate quibbling in defence of frauds, Britain will not for some time witness the complete extirpation of sophistication.

Perhaps the presence of the seeds of corn-cockle, darnel, ergot, &c., in flour, is more apt to occur than that of any adulterant purposely added. Due attention is here called to the examination of yeasts by microscopic and biological tests.

The author shows that, contrary to what may be almost called a superstition, white bread is more nutritious than the so-called whole-meal breads. The reason of this is that bran contains no gluten. Whole-meal bread, further, by the irritating action of the bran, accelerates the peristaltic movement of the bowel. Hence an excess of unutilised nitrogenous matter is found in the excreta of persons who have been fed on brown breads. The irritation of the bran may occasion unpleasant, and even dangerous, diarrhoea.

Mr. Jago dwells, in a very instructive and convincing manner, on the sanitary defects of urban bakeries,—on their underground situation, their defective ventilation, their frequent proximity to privies and other sources of nuisance. Nor does he forget to show the importance of kneading by machinery in place of hand-labour, which involves certain features most unappetising and possibly anti-sanitary. In the interest alike of the consumer and the working-baker, underground bakeries and hand-labour in kneading should be superseded. In these days of gas-engines, and of the electric transmission of power, this can be done without burdening the master-baker.

Mr. Jago's work is the more welcome because alien bakers succeed in finding a footing in this country—a fact unpleasant to all who believe in the good old principle "Britain for the British," and especially to all who have had the opportunity of closely observing Continental nastiness as existing in most countries except Holland.

We hope that the "Text-book of the Science and Art of Bread-Making" will be widely circulated and carefully studied."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxi., No. 3, July 15, 1895.

Nominations.—As correspondent of the Section of Anatomy and Zoology, Sir William Flower was elected, *vice* Prof. van Beneden. Prof. Ramsay was elected a correspondent for the Section of Chemistry, *vice* Dr. E. Frankland. Singularly enough, Prof. Mendeleeff received only one vote.

Deposit of Aluminium and Potassium Phosphate, and on the Genesis of these Minerals found in Algeria.—Ad. Carnot.—The deposit in question is found in the territory of Misserghin, near Tour Combes. It is found in a cavern of no considerable extent. It contains: Phosphoric acid, 35.17; alumina, 18.18; potassa, 5.80; ammonia, 0.48; lime, 0.31; silica, 11.60; water, with a little organic matter, volatile at 100°, 13.40; do. 100—180°, 10.55; do. at redness, 4.35; magnesia, fluorine, chlorine, sulphuric acid, traces; total, 99.84. All the facts observed may be explained by the infiltrations of water.

Absorption-spectrum of Liquefied Air.—Professors Livinge and Dewar.—(See p. 65).

Action of the Infra-red Rays upon Silver Sulphide.—H. Rigollot.—This paper will be inserted in full.

Detection and the Presence of Laccase in Plants—G. Bertrand.—The author has discovered laccase in beetroot, carrots, and turnips, in the tubers of dahlia and potatoes, in asparagus, in lucerne, trefoil, rye-grass, in plums, pears, quinces, and chestnuts, and in the flower of the gardenia.

Essence of Linaloe.—Ph. Barbier and L. Bouveault.—The essence in question contains diatomic and tetratomic terpenes, methylheptenone, licareol, licarhodol, and sesquiterpene.

MISCELLANEOUS.

Distinction between Coniin and Nicotin.—G. Heut (*Archiv. der Pharmacie*).—These substances behave differently with phenolphthalein. If we add to nicotin, dissolved in dilute alcohol of 0.95 to 0.96 sp. gr., a drop of a saturated solution of phenolphthalein, the liquid is not coloured red, as it is at once in case of coniin.

The German Association of Naturalists and Physicians.—We learn that the 67th Congress of this Association will be held at Lübeck from September 16th to 23rd. Scientific and medical men of all nations are invited, but the proceedings will be conducted exclusively in the German language. The subjects treated of are resolved into two main groups, that of the natural sciences and that of medicine. The former resolves itself into three subordinate groups. The first of these includes the sections for mathematics, astronomy, physics, chemistry, agricultural chemistry, agricultural experiments, and the lore of instruments. The second comprises the sections for mineralogy, botany, zoology, anthropology, and geography. In the third group are the sections for instruction in mathematics and natural science. A great advantage of the German Association is that it is not encumbered with a section for political economy, a subject for which there is ample scope elsewhere.

Australasian Association for the Advancement of Science.—The Seventh Session of the above Association will be held in Sydney, from the 3rd to the 10th January, 1897, under the Presidency of A. Liversidge, M.A., F.R.S., Professor of Chemistry, University of Sydney. The Presidents and Secretaries of the Sections are as follows:—

Astronomy, Mathematics, and Physics.—R. L. J. Ellery, C.M.G., F.R.S., Government Astronomer, *Viç.*, President; R. Threlfall, M.A., Professor of Physics, and J. Arthur Pollock, B.Sc., Demonstrator in Physics, Sydney University, Secretaries.

Chemistry.—T. C. Cloud, A.R.S.M., F.C.S., Manager Wallaroo Copper Works, South Australia, President; W. M. Hamlet, F.C.S., F.I.C., Government Analyst, N.S.W., Secretary.

Geology and Mineralogy.—Captain F. W. Hutton, M.A., F.R.S., F.G.S., Director of Canterbury Museum, and Lecturer in Geology, Christ Church, New Zealand, President; T. W. E. David, B.A., F.G.S., Professor of Geology and Physical Geography, Sydney University, and E. F. Pittman, A.R.S.M., F.G.S., L.S., Government Geologist, N.S.W., and Lecturer in Mining, Sydney University, Secretaries.

Biology.—T. J. Parker, B.Sc., F.R.S., Professor of Biology, Otago University, Dunedin, New Zealand, President; W. A. Haswell, M.A., D.Sc., F.L.S., Professor of Biology, Sydney University, and J. H. Maiden, F.C.S., F.L.S., Curator, Technological Museum, Sydney, and Superintendent of Technical Education, N.S.W., Secretaries.

Geography.—H. S. W. Crummer, Secretary of the Royal Geographical Society of Australasia (N.S.W. Branch), Secretary.

Ethnology and Anthropology.—A. W. Howitt, F.G.S., Secretary for Mines, Vic., President; John Fraser, B.A., LL.D., Sydney, Secretary.

Economic Science and Agriculture.—R. M. Johnston, F.L.S., Government Statistician, Tasmania, President; Walter Scott, M.A., Professor of Greek, Sydney University, and F. B. Guthrie, F.C.S., Consulting Chemist to the Department of Agriculture, N.S.W., Secretaries.

Engineering and Architecture.—H. C. Stanley, M.I.C.E., Chief Engineer, Southern and Western Railway Lines, Queensland, President; J. W. Grimshaw, M. Inst. C.E., M.I. Mech. E., &c., Supervising Engineer, Harbours and Rivers Department, N.S.W., Secretary.

Sanitary Science and Hygiene.—Hon. Allan Campbell, M.L.C., L.R.C.O., South Australia, President; J. Ashburton Thompson, M.D., Chief Medical Inspector, Board of Health, N.S.W., Secretary.

Mental Science and Education.—John Shirley, B.Sc., District Inspector of Schools, Brisbane, Queensland, President; Francis Anderson, M.A., Professor of Logic and Mental Philosophy, Sydney University, Secretary.

Communications and Papers for the Meeting, or inquiries, may be addressed to the Permanent Hon. Secretary, The Chemical Laboratory, The University, Sydney, N.S.W.

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Applications should be endorsed "Chemical Department."

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THE CHEMICAL NEWS.

VOL. LXXII., No. 1864.

NOTE ON THE HEXYLENE, $C_{12}H_{12}$, AND HEXYL-HYDRIDE, $C_{12}H_{14}$, DERIVED FROM MANNITE BY REDUCTION WITH HYDRIODIC ACID.*

By J. ALFRED WANKLYN.

TO-DAY is published, in the *Philosophical Magazines*, by Cooper and myself, an investigation of American petroleum parallel with our investigation of Russian kerosene. The hydrocarbons existing in American petroleum are members of the marsh-gas family, as was shown by the classical researches of Cahours and Pelouze, dating back to the years 1862 and 1863.

We now show that these marsh gases rise by increments of 7, and not 14 as has hitherto been maintained. Our investigation is at present confined to the more volatile part of the American oil, and we exhibit seven consecutive terms.

Having in our hands the corresponding terms of the Russian and American series, we are in a position to make a comparison of the physical characters of the two sets of liquids.

One of the most obvious facts brought out by this comparison is, that the Russian hydrocarbon is always a little heavier than the American with the same carbon-condensation. The increment of density is about 0.025 to 0.035.

More than thirty years ago, when I was working with Erlenmeyer, it fell to my lot to investigate the two hydrocarbons, hexylene and hexyl-hydride derived from mannite. Our account of these substances is published in the *Journal of the Chemical Society* for the year 1863, in our conjoint paper entitled "On the Hexyl Group."

It happens that by accident (although the sp. gr. of hexylene was determined with great care, in a thoroughly satisfactory manner) it was never published. I now place it on record.

The specimen of hexylene was prepared in the laboratory of the University of Edinburgh, by decomposing the iodide of hexyl (from mannite) by alcoholic solution of potash. The purity of the hexylene was shown by very satisfactory combustions of the substance; and here the remark may be made that good combustions afford decisive evidence of purity in a case of this kind, where no question of the presence of neighbouring homologues can arise.

Two determinations of sp. gr. at 4.8° C. and 45.5° C. were made thus:—

Sp. gr. at 4.8° = 0.6972
" 45.5° = 0.6604.

water at 4° C. being taken as unity, and the expansion of the glass being allowed for.

The sp. gr. of hexyl-hydride is given in our paper published in 1863, as 0.6645 at 16.5° C.

In the year 1864 I prepared the substance again, and made another determination of the sp. gr. at 0° C., and found it to be 0.6759; and, taking into account the circumstance that the temperature is lower than that in the former experiment, it is corroborative of the former.

By a simple calculation we are able to compare the sp. gr. of hexylene at 0° with that of hexyl-hydride at the same temperature:—

Sp. gr. of hexylene, $C_{12}H_{12}$, at 0° = 0.7017
" of hexyl-hydride, $C_{12}H_{14}$, at 0° = 0.6759

Difference = 0.0258

* In this paper the atomic weight of carbon is written as 6.

It would thus appear that—whether the hydrocarbons are extracted by fractional distillation from a complex mixture of homologues, such as petroleum, or whether they are obtained by such a process as reduction of polyatomic alcohols with hydriodic acid—the relation between the sp. gr. of C_nH_n and the sp. gr. of C_nH_{n+2} is the same.

August 1, 1895.

CONCERNING FUMING SULPHURIC ACID.

By R. W. HILL.

THE so-called Nordhausen or fuming sulphuric acid, $H_2S_2O_7$, is a compound of a molecule of ordinary sulphuric acid, H_2SO_4 , with a molecule of sulphuric anhydride or sulphur trioxide, SO_3 . By heating the fuming acid, the molecule of SO_3 is readily driven off.

Nearly every text-book on chemistry informs the student that this acid is still manufactured in Nordhausen, in Saxony, Germany. As a matter of fact, it was never manufactured in the said town, but in Goslar, a couple of miles from Nordhausen. At the present time, however, this acid is not manufactured at all either in or near that place; but this particular chemical branch is, practically speaking, monopolised by the large chemical concern of Johann D. Starck und Söhne, near Prag, Bohemia. They produce it in the old-fashioned manner by distilling green vitriol or ferrous sulphate,—



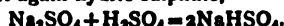
The anhydride thus given off is absorbed by rain-water or sulphuric acid, 66° Beaumé, thus producing fuming acid.

About twenty-five years ago Professor Cl. Winkler, of Freiberg, suggested the use of platinised asbestos as a "catalytic" substance for the union of pyrite—or brimstone—kila gas, SO_2 (sulphur dioxide), with the oxygen of air. The most favourable proportions are 29.6 vol. SO_2 + 70.4 vol. atmospheric air (containing 14.8 vol. oxygen); but for practical purposes it is advisable to employ a dry gaseous mixture of 25 per cent SO_2 + 75 per cent air; the dry anhydride does not attack cast- or tinned-iron. In some works in Russia and Germany this process is actually carried out on a commercial scale, with some modifications and improvements in the old idea.

In Kalk, near Cologne, Germany, Wolter's process is used, by distilling hydric sodic sulphate,—



The sulphate of soda is then treated with sulphuric acid, in order to get again hydric sulphate,—



About five years ago a German chemist produced the fuming acid from the ordinary sulphuric acid by means of an electric current. Carbon plates, about 1/4th inch apart, were immersed into sulphuric monohydrate, and an electric current passed through the fluid. The water of the acid is decomposed into hydrogen and oxygen, and the SO_3 is absorbed by the electrolyte, this forming fuming sulphuric acid, $SO_3 + H_2SO_4 = H_2S_2O_7$. As soon as a layer of sulphur is observed on the electrodes, the current is reversed. As far as the writer knows, this electrical process has never been tried on a commercial scale.

Manchester, August 3, 1895.

German Association.—Dr. H. Krüss will read a paper on a "New Procedure in Quantitative Spectral Analysis" at the forthcoming Congress of the German Association of Naturalists and Physicians. At the same Congress Prof. W. Ostwald will read a paper on the "Vanquishing of Scientific Materialism"; and Prof. Svante Arrhenius will explain the fluctuations of climate in Geologic Epochs by simultaneous modifications in the proportions of Carbonic Acid in the Air.—*Chemiker Zeitung*.

GOLD AND SILVER IN COPPER AND IN
COPPER MATTE.

By ERNEST A. SMITH, Assoc. R.S.M., F.C.S.

In a very interesting paper* "On a Uniform Method of Assay of Copper and of Copper Materials for Gold and for Silver," by Dr. Albert R. Ledoux, of New York City, the author referred to the discrepancies which often occur in the results obtained by different assayers working on the same sample, and suggested that some uniform method for assaying these materials should be arrived at, somewhat similar to the movement initiated by Prof. J. W. Langley, of Pittsburg, in 1888, which resulted in the general adoption of standard methods in the determination of carbon and other important elements in iron and steel. He proposed that a number of samples of gold- and silver-bearing copper material should be distributed to as many assayers as were willing to take part in the movement. In response to Dr. Ledoux's paper, a large number of establishments and assayers expressed their willingness to co-operate in the plan he proposed. The necessary samples were prepared by Dr. Ledoux, and distributed to the various parties co-operating. The results obtained have been received recently and tabulated, in a paper presented at the Florida meeting of the American Institute of Mining Engineers, and should be of interest to all those who have to assay similar materials in England. In discussing the various methods of assay in his paper, Dr. Ledoux draws attention to the fact that there is a divergence in the methods usually employed in the East and West for the assay of these copper materials. He points out that some of the Eastern public assayers use the "wet" method, which consists in treating one assay-ton (about 30 grms. or 500 grains) of the sample of copper borings or matte in a (No. 5) beaker with a mixture of 100 c.c. water and 50 c.c. nitric acid of sp. gr. 1.42. When the violent action has ceased, 50 c.c. more of nitric acid is added, and the solution heated until everything soluble is dissolved. It is then boiled until the free nitric acid is expelled; then diluted with 400 c.c. water and 5 c.c. sulphuric acid, and 10 c.c. of a concentrated solution of acetate or nitrate of lead added. The precipitate of lead sulphate is allowed to settle, filtered, and washed, and the filter and its contents are partially dried, then wrapped in thin lead-foil, and transferred to a scorifier. Cupellation is conducted in the usual manner.

This method is intended for the determination of gold, but enough silver may be present to allow the bead to be parted.

For silver the usual method in the East is to dissolve the sample in dilute nitric acid, as described above, and, before adding the lead salt, enough chloride of sodium is added to precipitate all the silver. The rest of the process is conducted as for gold.

In the West, the "all-fire" method of assay is employed almost exclusively.

At one works, ten portions of the samples, each of one-tenth assay-ton (about 2½ grms. or 50 grains), are scorified with 50 grms. of test-lead and a cover of 1 gm. of borax. The lead buttons obtained are cupelled separately, but the ten beads of precious metals obtained are weighed together. The cupels are then ground up and fused in five lots, of two cupels to each lot, with—

Litharge.. ..	90 grms.
Boron glass ..	50 "
Soda carbonate ..	50 "
Argol	3 "

The silver obtained, after cupellation of the resulting lead buttons, is added to that from the first assay. All the beads are then parted for gold.

Dr. Ledoux remarks that each of these methods in the

hands of assayers skilled in its application will produce fairly uniform results, yet any assayer running the two methods side by side will get divergent figures for gold. It is stated that the results obtained by this method are usually higher than those obtained by the "wet" method. For mattes the same method is employed, but sometimes a second scorification is necessary, which is usually performed in a 2½-in. scorifier, with the addition of lead to make up the total to 35 grms.

The necessary samples distributed to the various assayers were prepared in the following manner:—

Copper Matte.—A carload of matte was put through a Blake crusher, then automatically sub-divided into tenths by a "Taylor and Brunton" sampler, and one-tenth passed through Cornish rolls, and then through a 12 mesh screen. This was again sub-divided by an automatic sampler into tenths, and a final tenth, representing 1 per cent of the original lot, was finished by hand sampling on an iron floor until 100 lbs. remained. This was pulverised to pass a 40-mesh screen, and then thoroughly mixed and divided, in the presence of an assistant, for distribution to all those co-operating.

Copper Borings.—These were taken from a lot of anodes, the dip samples from several batches having been united, re-melted, and cast into a plate, which was proved by assay to be of uniform quality in its different parts. Borings from this plate were intimately mixed and divided in the presence of an assistant.

The samples were stated to have approximately the following compositions:—

Copper Matte.

Copper ..	50 to 60 per cent.
Gold ..	2 to 3 ozs. per ton.
Silver ..	100 to 150 " "

Copper Borings.

Copper ..	—
Gold ..	0.20 to 0.50 ozs. per ton.
Silver ..	140 to 180 " "

The detailed methods employed in each case are given in the paper presented to the Institute at the Florida meeting, and are substantially the same as those described. The results returned by the various assayers are as follows:—

Returns for Sample of Copper Matte.

	SILVER.		GOLD.		COPPER.		
	Ozs. per ton.		Ozs. per ton.		Per cent.		
	Direct scorifica-	Com- bined wet scorifica- tion.	Direct scorifica-	Com- bined wet and scorifica- tion.	Electro-deposi- tion method.	Cyanide method.	Iodide method.
1.	127.00	130.68	2.22	2.310	55.08	54.80	55.00
2.	135.38	127.60	2.35	2.240	55.17	53.70	
3.	129.99	125.20	2.33	1.850	54.96	52.72	
4.	131.89	129.72	2.41	2.260	55.04	50.55	
5.	128.95	123.03	2.09	2.325	54.50	54.37	
6.	127.60	125.31	2.22	2.215	54.86	50.75	
7.	128.75	128.06	2.27	2.240	54.60		
8.	122.88	128.27	2.28	2.260	55.08		
9.	131.22	125.95	2.29	2.050			
10.	126.80	128.70	2.26	2.160			
11.	127.44		2.36	2.270			
12.	127.02		2.27				
13.	128.70		2.33				
14.	130.42						
Means	128.86	127.25	2.28	2.198	54.91	52.81	55.00

One "crucible" assay gave:—

123.60 ozs. of silver per ton.
2.26 " gold "

* Read before the Bridgeport Meeting of the American Institute of Mining Engineers, October, 1894.

One combined "wet and crucible" assay gave:—

126.20 ozs. of silver per ton.
2.09 " gold "

Returns for Sample of Copper Borings.

	SILVER. Ozs. per ton.		GOLD. Ozs. per ton.		COPPER. Per cent.	
	Direct scorification.	Combined wet and scorification.	Direct scorification.	Combined wet and scorification.	Electro- deposition method.	Cyanide method.
1.	159.33	155.34	0.30	0.29	97.45	97.98
2.	159.68	160.78	0.32	0.24	97.04	
3.	164.35	156.31	0.35	0.22	98.19	
4.	159.12	148.50	0.40	0.205	98.46	
5.	147.40	157.30	0.35	0.21	97.50	
6.	155.75	156.92	0.35	0.28	97.37	
7.	164.05	157.04	0.30	0.24		
8.	154.40	153.65	0.40	0.317		
9.	156.90	161.40	0.37	0.30		
10.	160.63	156.10		0.25		
11.		156.97		0.22		
12.		159.67		0.22		
13.		156.72		0.501		
14.		159.27		0.40		
15.		148.78		0.26		
16.		159.00		0.28		
Means	158.16	156.49	0.35	0.277	97.66	97.98

One combined "wet and crucible" assay gave:—

161.35 ozs. of silver per ton.
0.42 " gold "

From the above tables the differences between the highest and lowest results returned are as follows:—

For Copper Matte.

	Direct scorification.	Combined wet and scorification.
Silver, ozs. per ton	12.50	7.65
Gold " "	0.320=6.4 dwts.	0.475=9.5 dwts.

For Copper Borings.

	16.95	12.90
Silver, ozs. per ton		
Gold " "	0.100=2.0 dwts.	0.296=5.92 dwts.

As Dr. C. B. Dudley remarks (in a paper read before the Chemical Section of the Engineers' Society of Western Pennsylvania, 1892):—"There are four main causes of error to which may be attributed the discrepancies in analysis between the results of different workers:—

1. The sample may not be uniform in composition, although supposed to be so.
2. The degree of purity of the chemical reagents always varies.
3. There is a "personal error" in manipulation, and there are various causes which prevent any particular method from being carried out in the usual way.
4. The results given by each method may be regularly higher or lower than the truth."

The first cause of error is one which frequently occurs in commercial samples, and would lead to the suggestion that more uniform methods of sampling be adopted for the various materials under treatment, although in the copper materials under discussion the discrepancies are probably due in a very minor degree to errors of sampling, and much more probably due in most cases to careless work and the use of inaccurate methods of analysis and assays. For assays in which assay lead is employed it is a matter of importance to take into account the amount of silver present, and to test every fresh sample of lead received for silver, as test-lead supplied as being "free from silver" can never be relied upon. Gold is invariably present (see experiments by Richard Smith, *Phil. Mag.*, Feb., 1854) in lead, but generally in such minute quantities

that it may be disregarded. The question of the silver in the lead used for the assay is often disregarded by assayers—a fact which may account for some of the discrepancies in the quantity of silver present in the copper materials operated upon.

Other, and perhaps more important sources of error, are the temperature at which the cupellations are conducted and the subsequent treatment of the buttons in the "parting" operation. Many assayers treat the buttons in one acid only in the "parting" process, and in some cases do not hesitate to use strong acid instead of dilute. The discrepancies may also be due to the want of a sufficiently accurate balance, a piece of chemical apparatus which is not always kept in the most perfect condition at metallurgical works. The errors likely to occur from this source cannot be too strongly impressed, when we bear in mind the comparatively small quantity of material operated upon, and the large increase in the error when the results are calculated to represent a ton of material.

Mr. J. W. Westmoreland, an assayer with considerable experience in the assay of copper materials, in referring to the assay of gold in bar copper (*Fourn. Soc. Chem. Ind.*, Feb. 27, 1886), remarks that "the general tendency is for the gold produce to be low, sometimes to a serious degree. . . . I believe this is due to some extent to the insufficient weight of material operated upon." In using $\frac{1}{2}$ oz. (240 grains) of copper chips for assay an error of 0.001 grain in the weight of the gold would amount to 3 dwts. of gold per ton (of 2240 lbs.) of copper. In the case of 1 oz. (480 grains) of copper chips, 0.001 grain would represent 14 dwts. per ton, but by careful weighing this could be reduced one-half, or to 18 grains per ton. He also remarks that "one assayer made his gold assay on 100 grains of copper chips. In this case 0.001 grain in the weight of the gold, representing 6.5 dwts. per ton; and it must be remembered that the value of this gold varies from 2/- to 3/6 per dwt.; hence the necessity for careful and accurate work."

The results collected by Dr. Ledoux are extremely interesting, and should be of value to all those engaged in assaying copper materials for silver and for gold.

Royal School of Mines, London.

NOTE ON THE PURIFICATION OF GLUCINUM SALTS.*

By EDWARD HART,

TWENTY years ago I found glucinum in a clay brought to Dr. Drown's private laboratory, in Philadelphia, for analysis. The experience gained then in making the separation from alumina showed clearly that none of the methods then known gave a satisfactory separation. In dissolving the carbonate we found that alumina also dissolves, and that in treating the oxides with solution of ammonium chloride, alumina as well as glucina dissolves.

In beginning the purification of glucina from beryl, which I have undertaken for a more careful study of the metal and its alloys, I determined, if possible, to prepare it in some other way than by the use of the time-honoured ammonium carbonate method, which, besides giving a material of doubtful purity, is expensive and tedious. Such a method has been found based on the properties of the mixed sulphates from beryl, and which seems not to have been used for this purpose. Perhaps it will be best to describe the method now used in full, without describing the failures through which the work passed.

The powdered beryl is first fused with mixed carbonates, and then ground and washed with water. The powdered mass is then mixed with sulphuric acid and

* Read at the Boston Meeting of the American Chemical Society, December 28, 1894.

evaporated to make the silica insoluble. The sulphate solution obtained from this material is evaporated and treated with an excess of potassium sulphate. Alum crystallises out, and is purified by re-crystallisation. The mother-liquor contains the glucinum along with the iron and alkaline sulphates. Potassium chlorate is added in excess, and the solution heated to peroxidise the iron. Sodium carbonate solution is now added, little by little, the solution being boiled after each addition until a filtered sample shows no yellow colour. The whole solution is then filtered, and the glucinum which will be contained in the filtrate is precipitated by further addition of sodium carbonate.

The method, of course, depends upon the fact that it is impossible to throw down the glucinum until the greater part of the acid has been saturated, the glucinum remaining in solution as basic sulphate. Iron and aluminum, on the contrary, are easily separated. Some care is needed in order to get rid of the last trace of iron, which persistently remains in solution until the point at which the precipitation of glucinum begins is almost reached.

A sample prepared in this way was perfectly soluble in hydrochloric acid, gave no reaction for iron with potassium ferrocyanide, was completely soluble in an excess of ammonium carbonate and caustic potash. The ammonium carbonate solution gave no precipitate on the addition of ammonium oxalate. The method is exceedingly simple, convenient, and cheap, and leaves nothing to be desired. — *Journal of the American Chemical Society*, xvii., 604.

ON THE FLUORESCENT SPECTRUM OF ARGON DESCRIBED BY PROFESSOR BERTHELOT.

BERTHELOT has submitted a specimen of argon sent him by Professor Ramsay to the action of the effluve. In the spectrum of the fluorescent light Berthelot was able to distinguish four lines, the wave-lengths of which, as measured with a spectroscope of low dispersive power, were as follows:—

579	millionths	..	..	..	m.m.
547	"	..	..	..	—
438	"	..	..	..	—
436	"	..	..	..	—

The limit of error was given as 3 to 5 of the last figures.

The line 579 made the impression of a double line, as also 547. Besides there were also bands in the green and the violet, and especially in the red and the orange, the feeble illumination of which did not admit of a determination of the wave-length.

Berthelot ascribes the observed lines to argon, and thinks that he can recognise the following lines indicated by Crookes; the degree of brightness of which is shown by the number in a bracket, where (10) expresses the greatest brightness.

574'06	..	..	..	..	..	(6)
555'70	..	..	..	..	..	(10)
549'65	..	..	..	..	..	(8)
433'35	..	..	..	..	..	(9)
430'05	..	..	..	..	..	(9)

It is, in the first place, highly improbable that among the numerous bright lines of the argon spectrum only these should be left under the action of the effluve. Why, e.g., did not the lines—

603'8	..	..	..	..	..	(8)
565'1	..	..	..	..	..	(9)
561'0	..	..	..	..	..	(9)
518'58	..	..	..	..	..	(10)

make their appearance?

The interpretation of Berthelot's observations is probably this: That he has observed the spectrum of mercury, and probably traces of the nitrogen spectrum.

The brightest lines of the mercurial spectrum, according to Thalén are—

578'96	..	..	..	..	..	(10)
576'81	..	..	..	..	..	(10)
546'06	..	..	..	..	..	(10)
435'81	..	..	..	..	..	(10)

and agree with Berthelot's value as closely as might be at all expected. Thalén's first two lines correspond to line 579, seen double by Berthelot. We should ascribe Berthelot's line 438 to mercury, and 436 to nitrogen, which has a bright band at 734'60.

We have further satisfied ourselves, by our own observations, that at high pressures a small addition of nitrogen to argon suffices to suppress almost entirely the argon spectrum.

The bands observed by Berthelot in the red, yellow, green, and violet have probably belonged to nitrogen.

We have repeatedly prepared argon, and in some cases we have also obtained a mercuriferous gas which showed Thalén's four above-mentioned lines in full lustre. The conditions under which the metallic mercury used in the apparatus is taken up by the gas we are not yet able to give, but acetylene seems here to play a part which in Berthelot's experiments may have been formed from the accompanying benzene vapour by the action of the effluve. — *Liebigs Annalen*, cclxxvii., p. 230.

QUANTITATIVE ANALYSIS OF GALENA.

By P. JANNASCH and H. KAMMERER.

ONE of the present writers has formerly proposed several methods for the analysis of galena. The precipitation of the alkaline (sodium) solution of the sulphide oxidised to sulphate by the direct addition of bromine, and also the precipitation by hydrogen peroxide of an ammoniacal solution in ammonium acetate, were recommended as especially simple; and, finally, as the most expeditious, the decomposition of the mineral in a current of bromine. The precipitation of the lead in an alkaline solution (potassic) by means of bromine was subsequently also used by L. Medicus, the halogen being applied in the form of vapour.

0·7 to 0·75 grm. of finely pulverised galena is placed in a porcelain capsule and moistened with dilute nitric acid, allowed to stand in the cold for some minutes, treated there with 10 c.c. of concentrated nitric acid, heated on the water-bath, and suitably evaporated. Nitric acid and water are added afresh, along with 10—15 drops of bromine, and heated, with frequent stirring, until all the sulphur is completely oxidised to sulphuric acid.

For the certain destruction of any bromate formed as a subsidiary product, we evaporate the saline mass three times with concentrated nitric acid until dry as dust. When this has been effected, the dry residue is boiled for a short time in a covered capsule with 60 c.c. of water and 20 c.c. of concentrated hydrochloric acid, so as to dissolve all the lead sulphate. The residual gangue is filtered off (using a tall beaker), the filter and the tube of the funnel are well washed with boiling water, incinerated, and weighed.

For precipitating the lead, the filtrate is heated to ebullition on a free flame until complete solution has been effected, and the liquid is poured into a previously prepared mixture of 25 c.c. water, 50 c.c. hydrogen peroxide, and 50 c.c. concentrated ammonia. The lead is thus precipitated as a fine yellowish red partially crystalline deposit, the composition of which will be determined subsequently. The whole is allowed to stand covered for several hours, with occasional stirring, filtered, washed

carefully with cold water, dried, and weighed in a platinum crucible as lead oxide.

For the determination of the sulphuric acid, the filtrate from the lead precipitate is evaporated on the water-bath until the odour of ammonia has disappeared; 5 c.c. of concentrated hydrochloric acid, and the same volume of alcohol are added, and the whole is gently heated for some time in order to re-generate certain quantities of persulphuric acid and to destroy with certainty any hydrogen peroxide still present. The sulphuric acid is then precipitated with the calculated quantity of solution of barium chloride. If this precaution is omitted, the results are much too low, in consequence of the solubility of barium persulphate.

Small impurities of a galena, consisting of copper, nickel, zinc, or arsenic, will be found in case of the hydrogen peroxide method in the ammoniacal filtrate, and after the separation of the sulphuric acid may be separately determined by barium chloride.—*Berichte*, 1895, No. 11, p. 1409.

ON THE RECOGNITION OF BLOOD SPOTS IN JUDICIAL CASES.

By FRIED. GANTTKE.

THE detection and demonstration of traces of blood upon rusty iron is known to be hindered, and in many cases rendered impossible, by the circumstance that it is not practicable to obtain crystals of hæmine, or to effect other reactions for the demonstration of blood from the substance which has been rendered insoluble by the ferric oxide. As a rule, in such cases, the result of the investigation—especially if it has had to be undertaken after prolonged contact with the rusty iron—is to this effect, that it has not been possible to show the presence of blood with certainty; but that this, in view of the great difficulty of recognising blood under such conditions, is no proof of the total absence of blood upon the article in question. But very often it is not merely to show the presence of blood, but quite as important to give a certain proof of its entire absence, i. e., to prove that the spots in question are certainly not due to blood.

For the latter purpose the behaviour of the blood-substance with hydrogen peroxide is a good means. If a drop of the solution of hydrogen peroxide is brought in contact with the slightest trace of the substance of blood, there occurs immediately a distinctly visible evolution of oxygen gas proceeding from the blood, and gradually increasing, so that the drop is very soon converted into a white frothy mass, which retains its froth-like character for a long time. This reaction is most distinctly manifested as follows:—

Upon a port-object—which for the sake of greater distinctness we lay upon black paper—we place a drop of the solution of the blood substance, or, if such a solution cannot be obtained, as in case of spots on rusty iron, a small portion of the scrapings of the rust, which is covered with a drop of a very weak alkaline water, and allowed to stand for some minutes to soften the blood substance. We then add a drop of solution of hydrogen peroxide, when, if the smallest trace of blood substance is present, relatively large gas-bubbles are evolved; in case of sanguiferous rust, we see that the development of gas does not proceed uniformly from all parts of the rust, but merely from certain points, i. e., from such only to which particles of blood adhere. The gas-bubbles, after some time, coalesce to a tender froth, which on the black paper appears snow-white, and which remains for some hours without melting away. It is a characteristic feature that this froth contracts from the margin of the drop towards the middle, so that the sharply limited white foam appears surrounded by a ring of clear liquid.

To mistake the phenomenon for ordinary air-vesicles is scarcely possible. Certainly, on moistening the rust with

the feebly alkaline water, single air-bubbles often appear, but they soon disappear if touched with a slender glass rod before the hydrogen peroxide is added.

If the reaction does not appear it is certain evidence that the rust-spots contain no blood. Inversely, however, the appearance of the reaction is no positive evidence of the presence of blood, since the animal fluids, e. g., pus, behave with hydrogen peroxide in the same manner as blood.

The reaction may also be usefully applied for the closer examination of the crystals of hæmine, if, as it sometimes happens, we are in doubt whether the crystals obtained are really those of hæmine. If we treat the microscopic preparation containing the crystals in the manner described above, there occurs at once a strong development of gas, whilst no change occurs if the crystals are other than those of hæmine.

The reaction is also suitable for a convenient preliminary examination of spots supposed to be blood. The age of the spots upon rusty iron does not seem to have any marked influence on the distinctness of the reaction; at least spots six months old showed the reaction as sharply as those freshly obtained.—*Zeit fur Anal. Chem.*, vol. xxiv., p. 159.

QUANTITATIVE DETERMINATION OF HYDRAZIN IN ITS SALTS.

By JULIUS PETERSON.

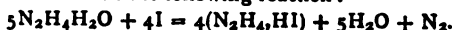
For this purpose Peterson utilises its well-known reductive action with Fehling's solution or with potassium permanganate.

Curtius (*Journ. Prakt. Chemie*, N. S., xxxviii., p. 418) recommends boiling the hydrochlorate with hydrochloric solutions of platinum chloride, and collecting the nitrogen evolved. The process takes place according to the equation—



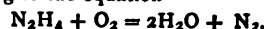
The author's experiments show that the proportion of nitrogen obtained is too high by about 1 per cent.

The volumetric method depends on the use of iodine, and is founded on the following reaction:—



It is applicable only for the hydrate, and is therefore of no universal importance.

Peterson's attempts to determine hydrazin with boiling Fehling's solution show that the process takes place according to the equation—



The author was not able to obtain constant results by titration; but a perfectly accurate determination of hydrazin can be effected by collecting and measuring the nitrogen liberated.

Peterson proceeds in the same manner as Strache in his determinations of the carbonyl-number.

The determination is effected as follows:—

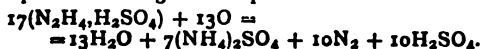
In a small flask, holding about 25 c.c., and capable of being closed with a caoutchouc stopper having two perforations, there is introduced a quantity of Fehling's solution, excessive in proportion to the substance to be used, and previously diluted with water to about 60 c.c., and heated to boiling. The stopper of the flask contains, in one of its perforations, a small glass tube, introduced from below, containing the weighed substance, and a small glass rod introduced from above. In the other perforation is a gas-delivery tube, through which the air is first expelled by watery vapour. When this has been effected, a measuring tube (filled with water previously boiled out) is placed over the gas-delivery tube, the lamp beneath the flask is withdrawn for a moment, and the little tube containing the substance is thrown into the

liquid by pushing in the glass rod. After a brief ebullition all the nitrogen is driven over, and can be measured in the usual manner. The tube used for introducing the substance contains about $\frac{1}{10}$ c.c. As it cannot be entirely filled, a correction of about $\frac{1}{10}$ c.c. is made in the volume of the nitrogen.

Hydrazin may also be determined by titration with potassium permanganate in a hot solution.

The titrations must be effected at 60° to 70°, and the solution must contain from 6 to 12 per cent sulphuric acid. We titrate in the ordinary manner. The titration is completed when, on further addition of the solution of permanganate, the liquid becomes more and more deeply coloured, when we titrate back with oxalic acid.

The oxidation, according to the author's experiments, takes place according to the equation—



The accuracy of the equation is proved by the consumption of the permanganate, the determination of the ammonia formed, as well as by measuring the nitrogen liberated.—*Zeit. Anorg. Chem.*, vol. v., p. 1.

ACTION OF THE INFRA-RED RAYS UPON SILVER SULPHIDE.

By H. RIGOLLOT.

It is known that silver sulphide, sensitive both to luminous and obscure radiations, may be employed as an electro-chemical actinometer. I have studied the action of the infra-red rays upon this compound, and have examined if the sensitiveness of silver sulphide to radiations is a thermo-electric action or depends on some other cause.

Two plates of silver sulphide, immersed in a dilute saline solution, formed an electro-chemical actinometer. The sulphuretted plates were prepared by electrolyzing a solution of sodium sulphide by a feeble current for two minutes. They were about 2 m.m. in width by 40 m.m. in length; they were paraffined on the sides facing each other, one only being exposed to the radiations studied. The actinometer, connected either to a Thomson galvanometer of the resistance of 25,000 ohms, or to a Lippmann electrometer, was successively exposed to the various radiations of a prismatic spectrum of the length of 55 m.m. from the rays D to G.

Under these conditions the sensitiveness of silver sulphide for the infra-red radiations is recognised to a great distance from the last visible radiations. The galvanometer still gives indications for the wave-length μ 1.32, and we find in the solar spectra the two minima at μ 0.96 and μ 1.16, and the chief maximum μ 1.04 as signalled by Langley. The electromotive force developed by the most active part of the infra-red spectrum, the slit having only the width of 1.4 m.m., is of 3 to 4 thousandths volt. In the visible spectrum the sensitiveness decreases very rapidly from the ray A to the ray F, becoming then negligible. The illuminated plate is always negative with reference to the other, whatever may be the solution employed.

In another series of experiments, in order to compare the thermo-electric effects with the luminous effects, there were employed plates of a greater breadth, about 6 m.m.; each of the two plates plunged into one branch of a U-tube of glass, containing a very dilute solution of silver nitrate or of sodium chloride. One of the limbs of the tube was surrounded with a glass jacket, and by filling the annular space with hot water we could establish between the two limbs of the U-tube a difference of temperature, ascertained by means of thermometers immersed in each limb. On the other hand, in the tube itself, the plate intended to be heated might be illuminated by a Benger burner, the luminous intensity of which corre-

sponds to that of a Carcel lamp, placed at the distance of 0.20 metre. The light fell upon the plate only for a very short time, the effect produced being instantaneous. The electromotive forces developed, whether by the difference of temperature or by light, were recorded as above.

It was observed that the light instantly produced a negative electromotive force of about $\frac{1}{1000}$ volt, and that, on heating, it was necessary to establish between the two plates a difference of temperature of 6° to 7°, to develop the same electromotive force, negative in silver nitrate, positive in sodium chloride.

On taking as liquids dilute solutions of NaBr, NaI, KBr, KI, K_2SO_4 , MgSO_4 , AgSO_4 , $\text{C}_2\text{H}_3\text{AgO}_2$, it was found that the illuminated plate is always negative with relation to the other, whilst the heated plate is negative only in solutions of salts of silver, and positive in solutions of the other salts tried.

The two series of experiments are certainly not identical, but I believe that they have a sufficiency of points in common, so that there being the difference of temperature necessary to develop an electromotive force of 0.002 volt, it would be difficult to admit that the action of the infra-red rays is merely thermic.—*Bull. de la Soc. Chim.*

REPORT OF EXPERIMENTS ON THE CHEMISTRY OF THE CYANIDE PROCESS, AND NOTES ON ITS WORKING.

NEW PROCESS FOR DETERMINING CYANIDES.

SOLUBILITY OF GOLD IN DOUBLE CYANIDES AND IN HYDROCHLORIC ACID.

PHENOLPHTHALEIN AS AN INDICATOR IN TITRATING POTASSIUM CYANIDE.*

By G. A. GOYDER, F.C.S.,
Analyst and Assayer to the South Australian School of Mines and Industries.

WHEN at the Government cyanide works at Mount Torrens in April last I noticed that the process in general use for determining the amount of "available" or simple cyanide of potassium, namely, titration of a known volume of solution by means of a standard solution of nitrate of silver, with the addition of a little potassium iodide to give a sharper end reaction, although it gave accurate results with ordinary solutions of potassium cyanide, in the presence of double cyanide salts the end reaction was ill-defined, and after making numerous experiments it appeared that in titrating the sump solutions, which contain much of their cyanogen as the double cyanide of zinc and potassium, the end reaction was not only ill-defined, but that the quantity of nitrate of silver required to produce a permanent turbidity increased with the dilution, with the temperature, and also with the amount of simple cyanide added to a greater extent than was calculated. Thus a sump solution, which titrated cold indicated 0.015 per cent of simple cyanide of potassium, after heating quickly on a water-bath indicated 0.07 per cent, or nearly five times as much. If, however, the heating and titration are done slowly much of the cyanogen is decomposed and lower figures obtained. A cold sump solution, to which nitrate of silver has been added to permanent turbidity on shaking, always clears on being heated. A 1 per cent solution of crystallised double cyanide of zinc and potassium on titration as above appeared to contain one-thirtieth of its total cyanogen as simple cyanide of potassium; on diluting to sixteen times the bulk it indicated one-third of the total as simple cyanide, and by further diluting to two hundred and fifty times the bulk the whole of the cyanogen appeared by titration to be simple cyanide.

* From the Sixth Annual Report of the Council, Adelaide 1895.

As regards the indefiniteness of the reaction, a sample of sump solution was divided into three equal portions. To No. 2 an equal volume and to No. 3 two volumes of distilled water were added, and these were given to an expert, well acquainted with the process, but not knowing how the solutions were made up, to test. He reported that No. 1 contained 0.04 per cent, No. 2 0.05 per cent, and No. 3 0.04 per cent of simple cyanide. It is evident that if No. 1 contained 0.04, No. 2 could only have contained half, and No. 3 one-third of that amount if the process were reliable.

Again, a sample of sump solution, which by the above test contained 0.02 per cent of simple cyanide, was strengthened up by pure cyanide of potassium, so that it was calculated to contain 0.09 per cent, but it now appeared to contain 0.15 per cent, so that at least 0.06 per cent of double cyanide was returned as simple cyanide. There may, however, be cases in which the addition of cyanide of potassium to sump liquors would not have this effect. Thus, supposing the solution to contain the double cyanide of iron and potassium, the addition of the proper amount of cyanide of potassium to this would produce ferrocyanide of potassium, $K_4FeC_6 + 2KCy = K_6FeC_6$, and on titration the cyanide of potassium would be found to have disappeared. In actual work, therefore, the results obtained by this method are only comparative, and it would indicate to some extent where a large excess of cyanide was used in lixiviation. If the solutions were alkaline the indications would again be interfered with, as will be shown by what follows.

I therefore modified the above process by adding a decided excess of caustic soda to the sump solutions before testing. If a precipitate is produced it is better to add, say, 10 c.c. of 5 per cent caustic soda to 20 c.c. of sump solution, shake, pass through a dry filter, and take 15 c.c. of the filtrate for titration. When this solution is titrated with nitrate of silver after the addition of a little potassium iodide the end reaction is exceedingly sharp; a decided excess of caustic alkali does not interfere, and the precipitate is not dissolved by heating. This method, however, not only indicates the simple alkaline cyanide present, but also the cyanogen present in the original solution as zinc-potassium cyanide. This process was used by me at Mount Torrens last April in watching the progress of lixiviation, and its indications gave much more exact information as to the progress than could be obtained by the ordinary process. According to an extract from the *Journal Chemical Industry*, Nov., 1894 ("The Cyanide Process"), W. R. Feldtmann (*Engineer and Mining Journal*, lviii., 1894, 218-219) has experimented with this process, and states:—"Addition of alkali to working solutions which have become somewhat weak in alkali brings up the strength by regenerating, i.e., decomposing the zinc cyanide, . . . so that, as a matter of fact, when the solutions are pretty strongly alkaline they contain no zinc as cyanide, but only as hydrate dissolved in alkali (zincate of potash, &c.)."

But I believe that caustic alkali is never added in large excess to the lixiviating solutions, and when added in small quantities the double decomposition would not be complete, and its amount could only be calculated by applying the laws of chemical mass action after finding the relative proportion of the double cyanide of zinc and potassium to caustic alkali, and the velocity of combination of the resulting salts. As in practice this problem is complicated by the presence of the double salts and caustic potash as well as other salts, its solution is probably impossible. It may, however, be taken for granted that when caustic alkali is added to a solution of double cyanide of potassium and zinc in molecular proportions the resulting solution will after a little time contain zincate of potash, cyanide of potassium, and the double salt.

Having recently found that hydrocyanic acid does not decolourise phenolphthalein, and that cyanide of potassium is alkaline to that indicator, while the double

cyanides are neutral, I have endeavoured to base on these reactions a new process for finding the amount of simple cyanide of potassium present in sump liquors, &c. In the presence of caustic alkali or alkaline carbonates this process could not be applied; bicarbonates do not interfere if the titration is made in a stoppered bottle with the necessary precautions. The titration is made by measuring 100 c.c. of sump solution, or solution after passing through the tailings, into a stoppered bottle, adding 1 c.c. of one-twentieth per cent phenolphthalein and running in decinormal hydrochloric acid till the pink colour is destroyed; 1 c.c. of the acid = 0.0065 per cent of cyanide of potassium present. By this reaction I have found that as a rule the sump solutions do not contain more than 0.0004 to 0.002 per cent of simple cyanide of potassium as a maximum amount, and that from this amount any caustic alkali or alkaline carbonate present must be deducted, so that it would appear that the solutions after passing the zinc boxes contain practically no simple cyanide of potassium, but that it is all converted into double salts. The following analysis of sump liquor from Mount Torrens confirms this opinion:—

Analysis of Sump Liquor from Mount Torrens after Passing Zinc Boxes.

Analysis.		Assumed composition of salts in solution.	
	Per cent.		Per cent.
Copper . . .	0.0030	Ferrocyanide of	
Zinc . . .	0.0178	potassium . .	0.0400
Iron . . .	0.0061	Copper-potassium	
Calcium . . .	0.0145	cyanide . . .	0.0072
Magnesium . .	0.0042	Zinc-potassium	
Potassium . .	0.0609	cyanide . . .	0.0676
Sodium . . .	0.0645	*Calcium carbonate	0.0362
Chlorine . . .	0.0875	*Magnesium carb.	0.0147
Cyanogen . . .	0.0477	*Potassium carb.	0.0025
Sulphuric acid		Potassium sul-	
radicle . . .	0.0401	phate . . .	0.0431
Carbonic acid		Sodium sulphate .	0.0241
radicle . . .	0.0333	Sodium chloride .	0.1442
Total . . .	0.3796	Total . . .	0.3796

* The carbonates would be in the solution as bicarbonates, but are here given as simple carbonates to facilitate comparison.

In addition to the above, the solution also contained traces of cobalt, mercury, silver, and gold. The flour mercury retained in the tailings from the battery is dissolved by the cyanide; some of it is again precipitated in the tailings by any soluble sulphide present in the solution, and the bulk of the remainder is precipitated in the zinc boxes. The quantity of mercury in the gold slimes from the zinc boxes is sometimes large in amount, and makes the fumes rising from them during ignition decidedly poisonous.

When discussing with Mr. L. W. Grayson, the manager of the Government plant at Mount Torrens, the alterations necessary to the old plant, I suggested that the 2-in. pipes leading from the bottom of the lixiviation vats, which are 8 ft. in diameter, should be reduced to 1-in., and that syphon bottles should be attached to the lower ends of these pipes by indiarubber tubing, the neck of the bottles being also furnished with indiarubber tubes, which could be directed into the openings of main lines of pipes leading respectively into the waste water tanks, the weak solution, and strong solution zinc boxes. These suggestions were carried out by Mr. Grayson, and it was found on testing them, that these small pipes, as soon as the solutions started running from the vats, became filled, and exerted a suction equal to between 4 ft. and 5 ft. of water—their vertical height—and thus hastened the rate of lixiviation, or permitted of tailings with a larger proportion of slimes being treated than would have been possible had the 2-in. pipes been retained, as the solutions could not be run through the tailings at such a rate as to fill 2-in. pipes,

and unless full they could not produce any suction. The progress of lixiviation can be readily judged by the appearance of the solution passing through the syphon bottles, and the rate of flow adjusted by taps at the lower end of the pipes near the bottles. With tailings of moderate fineness these taps are only one-third to one-half open to produce the requisite rate of flow.

The method of conducting the lixiviation suggested by me as suitable for the Mount Torrens plant was as follows:—During the filling of a vat the tap of the draw-off pipe was left open, and the syphon bottle removed, so that as much water as possible was drained off from the tailings. Each truck-load was levelled down with a rake until the vat was nearly full; the top was then levelled as accurately as possible, and strong solution of about 0.2 per cent cyanide of potassium to the amount of about one-third the weight of the ore was run in at the top. This solution, if the vat had been well and evenly filled with tailings, sank slowly and almost without a bubble, driving the interstitial air before it, and out by the draw-off tap at the bottom, whence it escaped with considerable force, and displacing the residual water which, after a time, escapes by the draw-off pipe in general quite clear and colourless. As soon as the air has all escaped and the water flows in a steady stream, the syphon bottle is attached and the stream directed to the waste water tank. After a further interval, the liquid in the bottle begins to assume a yellowish tint, when the stream is directed into the small zinc boxes, and the rate of flow reduced, so that the strong solution displaced by the addition of an equal bulk of weak or sump solution at the top, would flow through in the time found by experience to afford the best payable extraction. When the last of the weak solution has sunk to the level of the top of the tailings, wash water is added to displace it, and the rate of flow may be now increased to save time. When the solution in the syphon bottles has again become nearly colourless, the lixiviation process is finished. The importance of having the draw-off pipe at the lowest point of the vat, and having the bottom of the vat sloping towards it from all directions, may be noted here. In such a case the water and different solutions have scarcely any tendency to mix, and the line between them is sharp, and therefore the bulk of the residual water first coming out can be run away without danger of loss of gold, instead of being mixed with the cyanide solution, diluting it, and increasing its bulk. At the end, too, the last of the weak solution is displaced with much less admixture of water, and as the bulk of solutions in stock is always kept about the same, the care exercised in properly constructing the vats is more than repaid by a saving of gold and of cyanide.

(To be continued.)

A NEW BACTERIAL PIGMENT.

By ALBERT THORPE.

As the chemistry of the bacterial pigments is a subject which has been very little investigated, the present note may be of interest.

I have isolated the brown pigment from infusions of maize undergoing putrefaction by means of the *Bacterium brunneum*. This pigment is soluble in alcohol, and is precipitated from an alcoholic solution by the addition of water. The precipitate, after filtration, was re-dissolved in alcohol, and the solution evaporated to dryness at 40° C. The following figures were obtained on the analysis of this pigment:—0.4764 grm. of substance gave 1.358 grm. of CO₂ and 0.232 grm. of H₂O.

	Found.	Calculated for C ₁₈ H ₁₄ O ₃ .
Carbon	77.74	77.69
Hydrogen	5.62	5.03
Oxygen	—	17.28

From the foregoing percentage composition, C₁₈H₁₄O₃ represents the formula of this brown pigment.

The alcoholic solution of the pigment gave no characteristic absorption-bands when examined by means of the spectroscop.

This pigment is soluble in alcohol, ether, and chloroform, insoluble in water and carbon disulphide, and acids appear to destroy it.

NOTICES OF BOOKS.

Life and Labour of the People in London. Edited by CHARLES BOOTH. Vol. VI., Population Classified by Trades (continued). 8vo., pp. 383. London and New York: Macmillan and Co. 1895.

THIS work contains much interesting matter, but also much that cannot come under our cognisance at all.

The total number of persons employed in the manufactures of surgical, "philosophical"—we strongly object to this term—and electrical instruments is 8258, more than half of whom are engaged in the production of electrical appliances, and 2000 of whom are under 25 years of age.

As regards surgical instruments, we are not sorry to learn that the hospitals and the leading operators do not approve of importations from the Continent. Microscopes of German make are, on the contrary, highly appreciated. In this and the kindred trades a really good workman is at a premium.

Concerning the manufacture of spectroscopes, chemical balances, and other requisites for the physical and chemical laboratory, we believe that an increasing proportion are of German make. The same fact must, beyond doubt, be admitted concerning glass and porcelain scientific apparatus. In the coloured glass manufacture we find it remarked that an Italian or French working man might perhaps develop an artistic sense of his own, but this, apparently, an Englishman can rarely do. This is a fact gravely to be regretted. Concerning the pottery trade, we learn that "betting, even more than drink, is now the ruling extravagance."

The persons employed in the chemical arts amount to 5836, a portion of whom are merely manufacturers of blacking, of matches, and of "proprietary" medicines. The rank and file of the chemical workmen earn little more than 25s. per week. There is no complaint of unhealthiness, save in the white-lead works. Among the match-makers necrosis in the jaw is greatly decreasing. Still it is very desirable that the use of white phosphorus should cease entirely. Indeed the entire elimination of phosphorus in the match-trade, and that of white-lead in pigment-making, rank among the most important problems of chemical industry.

Concerning soap, we think that Mr. G. H. Duckworth goes too far in asserting without qualification that "the fats used are of the most disagreeable nature." What of the Russian and Australian tallows, the palm- and coconut oils? The total of the persons employed in this business, and in bone-boiling, candle-making, &c., amount to 2195, and their wages rarely exceed 30s. weekly.

The unsavoury businesses of the tanner, fellmonger, currier, furrier, &c., employ 15,739 persons. The men employed are accused—we fear truthfully—of a tendency to drink to excess. The employment, especially of those who prepare furs for the hatters, is unhealthy, and no type of respirator hitherto devised has been found suitable.

As for the textile trades we are, of course, most concerned with the dyeing and cleaning departments. Dyeing on the large scale, as applied to new goods, can scarcely be said to exist in London, though the garment dyer, once numerous, is gradually diminishing. Leaving out of the question provincial competition, the London garment dyer is now poached upon by the monopolist

draper and by the jobbing tailor. The number of persons employed in the trade is now given as 1946. Concerning health there is little room for complaint. Indeed, in the manufacturing districts of Yorkshire and Lancashire, it is a common saying that a dead dyer is as great a rarity as a dead donkey. The chief peril to the dyer and cleaner springs from the ignition or explosion of the vapour of "benzoline spirit." Two injurious substances encountered in the waterproofing business are sulphur chloride and carbon disulphide. Hitherto no method of obviating their hurtful effects, or of superseding them by means of any harmless substance, has been elaborated.

The general impression produced by a perusal of this work is far from pleasing. We see a number of trades declining, and in many others the average remuneration obtained by the workers is not sufficient for the demands of a healthy life.

The Manufacture of Aluminium Sulphate (Die Fabrikation von Schwefelsaurer Thonerde). By Dr. KONRAD W. B. JURISCH, Docent at the Royal Technical High School, of Berlin. Berlin: Fischer & Heilmann.

We have here a useful monograph of aluminium sulphate, or, as it is sometimes called, "concentrated alum." The author describes the raw materials, their sources, the process of manufacture, the properties and applications of the finished product, and the statistics of the trade.

Analyses are given of native sulphates from various parts of the world, the best being apparently that from Adelaide. The alum-shales and native alum-earths are correctly pronounced of little value for the manufacture in question.

The number of patents for the production of aluminium sulphate is truly appalling. But it is evident that the early attempts to use clays and felspar for the manufacture either of alum or of aluminium sulphate are being more and more restricted, since bauxite—a far preferable material—is now obtainable in increasing quantities. Cryolite ($6\text{NaF} \cdot \text{Al}_2\text{F}_6$) is indeed an excellent material; but the only locality where it is obtained in quantity and in full purity is Arsak, in the south of Greenland. A sample from Miasak was found not free from ferric oxide. Cryolite is at present used only at the Oeresund works, near Copenhagen, and at the Natrona works near Pittsburg, in Pennsylvania.

Eglington clay is mentioned as a raw material, but its composition is not stated. The product contains 0.15 to 0.20 per cent Fe, and is consequently unfit for the uses of the paper-maker and the tissue-printer. We fear that some confusion in terminology has crept in, since we have heard the name Eglington clay used as a synonym for gibbsite.

Bauxite is described as the leading material for the production of sulphate of alumina. The best quality is that from the neighbourhood of Belfast, as used by P. Spence and Spence Brothers of Manchester, and raised by the Irish Hill Mining Co. The best quality, the so-called "Gertrude-bauxite," contains only 0.53 per cent of Fe_2O_3 , whilst many French sorts contain upwards of 20 per cent of this very troublesome impurity.

In working up bauxites the process generally followed is that of Lechatelier, which consists essentially in ignition with soda, lixiviation with water, filtration, and precipitation with carbonic acid, which of course throws down aluminium hydroxide; filtration and re-solution in sulphuric acid, which on cooling yields the commercial "cake-alum." For the details we must refer to the work of Dr. Jurisch. The outlook of the manufacture is very fairly summed up in the words that the present task of the cake-alum maker is to produce regularly and certainly an aluminium sulphate as free as possible from iron, containing from 14 to 14.5 per cent Al_2O_3 , containing neither free acid nor excess of alumina, and giving a clear solution in water.

There is given an extended table showing the specific

gravities and the percentage contents of solutions of cake-alum from 1.005 to 1.341.

The basic sulphate $\text{Al}_2(\text{HO})_2(\text{SO}_4)_2$ is precipitated on dilution.

The impurities most dreaded in commercial cake-alum are iron and free acid. Samples containing from 0.003 to 0.01 per cent of iron are commonly said to be free from iron, though many dyers and tissue printers dread even these traces, in the case especially of pink and rose shades, and hence prefer ordinary alum. Traces of iron, not exceeding 0.05 per cent can be determined colorimetrically. The free acid in cake-alum rarely exceeds 0.5 per cent. It is allowed by the maker to remain, not on account of the difficulty of its removal, but to give the product a better colour. In presence of free acid, 0.05 per cent of ferric oxide does not occasion a yellowish colour.

The uses of cake-alum are as a mordant—or material for mordants—in dyeing and tissue-printing, in paper-making, in the sizing process, and in tawing hides (in these applications the absence of iron is most essential), and as a purifier for sewage and waste waters containing organic pollution. For this last purpose the presence of ferric sulphate—as in Spence's alumino-ferric cake—is not at all objectionable. We may remark that where hydrochloric acid is available, an aluminium hydrochlorate, obtained either from hydrargyllite or from iron sludge, is preferable to the sulphate for the treatment of sewage.

Dr. Jurisch, by the publication of this work, has conferred a substantial benefit upon the producers and consumers of cake-alum.

Cape of Good Hope, Department of Agriculture. Report of the Senior Analyst on the Analytical Laboratory for the Year 1894. Cape Town: W. A. Richards and Sons. 1895.

THE Analyst reports that the work of the Department has increased progressively from 47 in 1889 to 506 in 1894. The three Government Laboratories of Cape Town, that connected with the Adulteration Act, with the Department of Agriculture, and with the Geological and Irrigation Office, have been amalgamated.

The substances given in for analysis were very promiscuous, samples of milk being the most numerous. Of the 124 samples 42 were found to be adulterated, and of the 38 coffees 10 had been sophisticated. In case of milk, the fraud has consisted in skimming and in the addition of water. The milk of a cow, in an advanced stage of phthisis, showed:—Total solids, 9.39; milk fat, 2.60; solids not fat, 6.79; and water, 90.61.

The adulteration of coffee was solely with chicory, which in one case—from Kimberley—reached the alarming proportion of 67 per cent! One sample of whisky was totally factitious. The samples of pepper examined were all found to be genuine.

Of gold-quartz 54 samples were examined, of which 25 showed not a trace of gold. Of the samples received from Mashona Land two contained $\frac{1}{8}$ ounces per ton, and one as much as 6 $\frac{1}{2}$ ounces.

Three samples of coal were found to be of fair quality, and an anthracite from Xalanga, in Tembuland, is likely to prove of great value.

The only sample of nitre sent in was one from Prieska, containing 78.9 per cent of potassium nitrate.

A lode of sulphur in admixture with graphite may be valuable if the finder is not mistaken as regards its extent.

The waters were not satisfactory. That from the Gamtoos River Bridge is more saline than the Indian Ocean. Out of 23 samples of water only 5 were fit for use, 7 doubtful, and the rest polluted and unfit for use. Out of 81 samples of well-water 71 were bad, including 29 from Cape Town and its district.

The soils show generally a deficiency in phosphoric acid, and in many instances also in potash.

A sample of peat-ash from Durban was found exceedingly poor.

Two native barks contained respectively 25 and 26 per cent of tannin. If abundant they may be exported to advantage.

Two samples of Cape tea have been examined. These were not ordinary teas grown in Africa, but were obtained from native shrubs. They contained no theine or any similar alkaloid.

L'Industrie Chimique (Chemical Industry). By A. HALLER, Directeur of the Chemical Institute of the Faculty of Sciences of Nancy, Correspondent of the Academy of Sciences and the Academy of Medicine. Pp. 348. Paris, J. B. Baillière et Fils. 1895.

THIS compact work forms the first volume of a series entitled the "Encyclopædia of Industrial Chemistry and Metallurgy." It treats more especially of higher instruction in different countries; of the products of the heavy chemical industry, the works, and their recent improvements; of chemical and pharmaceutical products, especially the products little known or recently discovered; artificial colouring matters; essential oils, and raw materials for perfumery.

The first of these heads is of the deepest and most general interest. It is admitted that the German chemical manufacturers are constantly growing at the expense of those of France and Britain. The causes of this superiority are manifold; but first and foremost stands the organisation of the German Universities, who are here aptly pronounced to be "the makers of the national glory and prosperity." There is no restraint, no subjection to any narrow pre-arranged "syllabus." The professors enjoy that freedom of spirit which is most favourable to high culture, and which is not met with in any other country. The interference of the public authorities in questions of the *personnel* of a university is as restricted as possible. The universities, though dependent on the State and paid by it, enjoy an autonomy which enables them to choose their rectors, their deans of faculty, and their professors, and present them to the Minister of Public Instruction for formal nomination, and it is very rare for the Government to interfere with the choice of the *Senatus Academicus*.

To be called to the occupation of a chair it is not necessary to produce numerous certificates, to undergo depressing competitions which throw no light on the originitive power of the candidate. It is merely requisite for him to have given proof of originality in research, and to have manifested himself a pioneer in Science. A *Rector Magnificus*—a dignitary essentially equivalent to the Chancellor of an English University or to the Lord Rector in Scotland—has not to undergo, like the latter, election on the principles of political faction, or to be selected by a body consisting mainly of half-pay officers. A candidate for a professorship of experimental science has not to be "heckled" on points of theological controversy or to sign a confession of faith. The student has not to waste precious time and priceless brain-power in preparing for successive examinations, and the inventor has not to meet the interference of alien patentees who obtain patents without any intention of practising them upon German soil. To meet with competition so arranged our industrialists, bound as they are by a vicious system, would have to be superhuman.

It is interesting to find that the institutions of higher instruction cost only 5d. annually per head of the population. Are they not an incomparably better investment than the Board Schools of Britain?

Besides the twenty-two Universities of the German Empire, the Polytechnic Schools of Aix-la-Chapelle, Karlsruhe, Brunswick, Charlottenburg, Darmstadt, Dresden, Hanover, Munich, Stuttgart, the Mining Schools of

Berlin, Clausthal, and Freiberg, and the Agricultural Schools, are almost all well provided with laboratories where researches in pure chemistry are carried on along with studies in applied chemistry. And these institutions are confided to men of proved scientific authority, who make it their task not merely to initiate the young students in the practice of chemistry, but to rouse in them the spirit of research and guide them into the track of discovery.

By means of the influx of foreign students, German science and German ideas are diffused, and at the same time German merchandise and German products. In the years 1891 and 1892 there were not fewer than 446 students of American nationality studying at German Universities; and not fewer than 800 at the Polytechnics, the Mining and Agricultural Colleges of Germany. Shall we reconsider our ways, or shall we go on examining and being examined, until we arrive at a universal collapse such as our Chinese models and forerunners in examinationism have just reached?

CORRESPONDENCE.

BORAX AND STANDARD ACID SOLUTIONS.

To the Editor of the Chemical News.

SIR,—If our method of standardising acid solutions by means of borax is not new, as Mr. Droop Richmond says in *CHEMICAL NEWS*, vol. lxxii., p. 5, we at least have discovered it independently, and have done something to make it better known.

Our aim was not to show to what accuracy the method could be carried, but rather to point out that, without taking any special precautions, results of very fair accuracy could be obtained.

We do not consider it necessary to estimate the water of crystallisation if large clear crystals of borax are used, but as this may be open to question, we intend making further experiments to test this point. The results we obtained were certainly good enough for ordinary analytical work. One of the results is evidently a little incorrect, but probably through no fault of the method employed. We do not know why Mr. Richmond should have dragged carbon dioxide into the question.—We are, &c.,

E. P. PERMAN.
W. JOHN.

University College, Cardiff,
August 6, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Zeitschrift für Analytische Chemie.
Vol. xxxiii., Part 6.

(This part has appeared only after vol. xxxiv. has already commenced appearing).

Wine Statistics of Germany. VII.—A continuation of a voluminous report interesting exclusively to the wine trade.

Acid Potassium Tartrate as a Fundamental Substance for Volumetry.—A. Bornträger.—The pure acid tartrate has come into use for standardising alkaline solutions, and is giving satisfaction.

Experiments on the Speed of Filtration of various Solutions.—R. Lezé.—From *Comptes Rendus*, cxiv., p. 1440.

On Pyrometry.—Various constructions have been discussed or proposed by Roberts-Austen (paper at Chicago International Congress, 1883), C. Gabb (*Stahl und Eisen*), Uehling and Steinbart (*Stahl und Eisen*).

A small Air Thermometer for Laboratories.—Lothar Meyer (*Berichte*, xxvi., 1047) proposes a modification, here figured, of Bottomley's thermometer (see *Phil. Mag.*, 1888).

Volumeter for Determining the Volumes of large Samples, especially Soils.—Tacke (*Zeit. Angewandte Chemie*).—Readers are referred to the originals for details.

New Form of Weighing Pipette.—H. Schweitzer. —From the *Journal of the American Chemical Society*.

Self-acting Apparatus for Filtration and for Washing Precipitates with Cold or Hot Water.—P. N. Raikow (*Chemiker Zeitung*).—This paper requires the two accompanying figures.

A Minimum Gas Blast.—Hugo Schiff (*Chemiker Zeitung*).—This paper also cannot be reproduced without the accompanying illustration.

Protective Capsules for Platinum Crucibles.—H. Petzilk. —The author uses platinum capsules, gilt without, so as to withstand smoking flames, of such a shape and size as to completely cover the bottom of the crucible as far as the flame extends.

Determination of Carbon in Iron.—A conspectus of the most general methods for determining the carbon contained in iron, as proposed by A. Ledebur (*Verein zur Beford. des Gewerbf. Fleisses*); Regnault, Jüptner, and Gmelin ("Handbuch für Eisenhütten Chemiker"); Sarnström, Ullgren and Elliott, McCreath, Rurup (*Chemiker Zeitung*); Barba (*Stahl und Eisen*); Langley, Blair, Dudley, and Shimer (*Zeit. Angewandte Chemie, Mining Journal*); Lorenz (*Zeit. Angewandte Chemie*); Woehler, Eggertz, Ukena (*Stahl und Eisen*).

Melting and Boiling Points of the Phenols and their Benzoates.—A. Béhal and E. Choay. —From the *Comptes Rendus*, cxviii., p. 1211.

Determination of Nitrogen.—W. F. Keating Stock. —From the *Analyst*, xviii., 38.

Determination of the Thioureas, and their Separation from the Sulphocyanides.—H. Salkowski (*Berichte*).—In solutions of pure thioureas the total sulphur is precipitated as silver sulphide by ammoniacal silver nitrate. It is filtered off, washed, and heated, first over the simple Bunsen flame, and then fused over the gas blast. All the silver sulphide is thus converted into silver, from the weight of which the quantity of thiourea is calculated. 2 atoms of silver represent 1 mol. of thiourea. For separating thioureas from the sulphocyanides, the clear solution is mixed with an excess of ammoniacal solution of silver. A mixture of silver sulphide and sulphocyanide is precipitated, though a part of the latter remains in solution. After some hours the conversion of the thioureas is completed, when the precipitate is filtered and washed. The filtrate is acidified with sulphuric acid, and the precipitate of silver sulphocyanide is allowed to stand in darkness. The washed precipitate is digested in the cold with solution of potassium cyanide until all the silver sulphocyanide is dissolved. After dilution it is filtered, and the washed silver sulphide is weighed as silver in the manner mentioned above. The filtrate is acidulated with sulphuric acid and heated on the water-bath until all the hydrocyanic acid is expelled. If this is delayed, silver sulphocyanide remains in solution. The silver sulphocyanide thus obtained, along with that which had been set aside in the dark, is filtered on a filter which has been dried at 105°. After filtering and drying at 105° the silver sulphocyanide is weighed.

Detection of the Fat of the Ox in Lard.—W. F. Keating Stock. —From the *Analyst*, xix., 2.

Determination of Hübl's Iodine Number.—W. Fahrion (*Chemiker Zeitung*, xvii., p. 1100).—The author observes that methylic alcohol is preferable to ethylic alcohol for the preparation of Hübl's iodine solution. The solution of sublimate-iodine in methylic alcohol certainly becomes weaker in time, but not to the same extent as the solution in ethylic alcohol. Fahrion shows also that along with the addition of iodine atoms to the double combinations of the non-saturated fatty acids there ensue other processes, so that in general the iodine number is found rather higher than would correspond to the proportion of non-saturated fatty acids in the oil. A high temperature and exposure to light increases the number considerably.

Determination of the Melting-point of Solids.—E. J. Bevan. —From the *Analyst*, xviii., p. 286.

Determination of Fatty Matter in Milk.—The process of Leo Liebermann and S. Szekeley has been verified and recommended by Long (*Pharm. Zeitung*).

Arrangement for a Rapid Approximate Determination of the Quantity and Purity of Carbonic Acid in Mineral Waters, &c.—Th. Kyll (*Zeit. Angew. Chemie*).—Apparently a hollow corkscrew ending in a three-way cock.

Chemistry of Vegetable Fibres.—C. F. Cross, E. J. Bevan, and C. Beadle. —From the *CHEMICAL NEWS*, lxxviii., p. 227.

Examination of the Ethereal Oils.—Schimmel and Co. —A very extensive paper, not suitable for abstraction.

Method for the Volumetric Determination of the Phosphoric Acid, Soluble in Water, contained in Superphosphates.—W. Kalman and K. Meissels. —Already inserted.

Determination of Uric Acid, and of the so-called Xanthine-substances in Urine.—E. Salkowski (*Centralblatt f. Med. Wissenschaft*).—This paper will also be inserted in full.

Detection of Glucose and other Cætohydrates in Urine.—K. Baisch (*Zeit. Physiol. Chemie*).—This paper will also be inserted in full.

Examination of Blood-pigment as to its Absorbent Power for the Violet and Ultra-Violet Rays.—H. Grabe. —Already inserted.

The Atomic Weight of Barium.—T. W. Richards (*Amer. Acad. Arts and Sciences*).—Already inserted.

MISCELLANEOUS.

The Drug and Chemical Trades Exhibition.—We have the pleasure of announcing that, on the 10th, 11th, 12th, and 13th of next month, there will be held in the Royal Agricultural Hall, N. (Islington), an Exhibition of the Drug, Chemical, and Allied Trades. The promoters, subscribers to the *British and Colonial Druggist*, hope to render this demonstration a periodically recurring display, so that it may bring under the notice of the trades and of their customers all improvements, new products, and procedures which may present themselves. The promoters admit that former exhibitions in connection with the drug and chemical trades have not proved successful. On the present occasion the management will not only be entirely new, but a general attendance of the trade is practically guaranteed, and most of the leading firms concerned have already promised their support to the undertaking, and intend to be represented. No department of our national industry and commerce requires to be more energetically and prudently supported than that in question. We hope that enlightened self-interest, not less than patriotism, will combine to ensure the success of the present Exhibition.

Award of the Hodgkins Prize of 10,000 Dollars to Lord Rayleigh and Professor Ramsay. — In March, 1893, it was announced by the Smithsonian Institution, in furtherance of the wishes of Mr. Thomas Hodgkins, who had presented a large donation to the Institution for the "increase and diffusion of more exact knowledge in regard to the nature and properties of atmospheric air, in connection with the welfare of man," that a prize of 10,000 dollars would be given for a treatise embodying some new and important discovery in regard to the nature and properties of atmospheric air. The competing treatises had to be sent in before the end of December, 1894. We have much pleasure in announcing that this prize has been awarded to Lord Rayleigh and Professor Ramsay for their treatise on the discovery of Argon.

Clay Filters, and their Use in Chemical and Bacteriological Laboratories.—W. Pukall (*Berichte*).—The author has produced filters which have not the soft sensitive surface of the Chamberland or the Berkefeld (Kieselguhr) filters, but have in a high degree the power of transmitting gases or liquids on the application of exhaustion from below or pressure from above. The filters consist of a suitable composition of china clays of different beds (aluminium silicate with quartz), which can be sharply burnt though remaining sufficiently porous. The construction recommended by Pukall is figured in the original.

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THE CHEMICAL NEWS.

VOL. LXXII., No. 1865.

THE SPECTRUM OF HELIUM.

By WILLIAM CROOKES, F.R.S.

IN the CHEMICAL NEWS for March 29th last (vol. lxxi., p. 151) I published the results of measurements of the wave-lengths of the more prominent lines seen in the spectrum of the gas from Clèveite, now identified with helium. The gas had been given to me by the discoverer, Professor Ramsay; and being from the first batch prepared, it contained other gases as impurities, such as nitrogen and aqueous vapour, both of which gave spectra interfering with the purity of the true helium spectrum. I have since, thanks to the kindness of Professors Ramsay and J. Norman Lockyer, had an opportunity of examining samples of helium from different minerals and of considerable purity as far as known contamination is concerned. These samples of gas were sealed in tubes of various kinds and exhausted to the most luminous point for spectrum observations. In most cases no internal electrodes were used, but the rarefied gas was illuminated solely by induction, metallic terminals being attached to the outside of the tube.* For photographic purposes, a quartz window was attached to the end of the tube, so that the spectrum of the gas could be taken "end on."

My examinations have chiefly been made on five samples of gas.

1. A sample from Professor Ramsay in March last. Prepared from Clèveite.
2. A sample from Professor Ramsay in May last. Prepared from a specimen of Uraninite sent to him by Professor Hillebrand. Gas obtained by means of sulphuric acid; purified by sparking.
3. A sample from Professor Ramsay in June last. Prepared from Bröggerite.
4. A sample from Professor Lockyer in July last. Prepared by a process of fractional distillation from a sample of Bröggerite sent to him by Professor Brögger.
5. A sample of gas from Professor Ramsay, "Helium Purissimum." This was obtained from mixed sources, and had been purified to the highest possible point.

In the following table the first four samples of gas will be called:—1. "Clèveite, R.;" 2. "Uraninite, R.;" 3. "Bröggerite, R.;" and 4. "Bröggerite, L." Only the strongest of the lines, and those about which I have no doubt, are given. The wave-lengths are on Rowland's scale.

The photographs were taken on plates bent to the proper curvature for bringing the whole spectrum in accurate focus at the same time. The spectrum given by a spark between an alloy of equal atoms of mercury, cadmium, zinc, and tin, was photographed at the same time on the plate, partially overlapping the helium spectrum; suitable lines of these metals were used as standards. The measurements were taken by means of a special micrometer reading approximately to the 1/100,000th inch, and with accuracy to the 1/10,000th of an inch. The calculations were performed according to Sir George Stokes's formula, supplemented by an additional formula kindly supplied by Sir George Stokes, giving a correction to be applied to the approximate

wave-lengths given by the first formula, and greatly increasing the accuracy of the results.

Wave-length.	Intensity.	
7065'5	5	A red line, seen in all the samples of gas. Young gives a chromospheric line at 7065'5.
6678'1	8	A red line, seen in all the samples of gas. Thalén gives a line at 6677 and Lockyer at 6678. Young gives a chromospheric line at 6678'3.
5876 0	30	The characteristic yellow line of helium, seen in all the samples of gas. Thalén makes it 5875'9, and Rowland 5875'98. Young gives a chromospheric line at 5876.
5062'15	3	
5047'1	5	A yellow-green line, only seen in "Helium Puriss." and in "Bröggerite, R." and "L." Thalén gives the wave-length as 5048.
5015'9	7	A green line seen in all the samples of gas. Thalén gives the wave-length 5016. Young gives a chromospheric line at 5015'9.
4931'9	3	
4922'6	10	A green line, seen in all the samples of gas. Thalén gives the wave-length 4922. Young gives a chromospheric line at 4922'3.
4870'6	7	A green line, only seen in "Uraninite, R." Young gives a chromospheric line at 4870'4.
4847'3	7	A green line, only seen in "Uraninite, R." Young gives a chromospheric line at 4848'7.
4805'6	9	A green line, only seen in "Uraninite, R." Young gives a chromospheric line at 4805'25.
4764'4	2	There is a hydrogen line at 4764'0.
4735'1	10	A very strong greenish blue line, only seen in "Uraninite, R."
4713'4	9	A blue line, seen in all the samples of gas. Thalén's measurement is 4713'5. Young gives a chromospheric line at 4713'4.
4658'5	8	A blue line, only seen in "Uraninite, R."
4579'1	3	A faint blue line, seen in "Uraninite, R." Lockyer gives a line at 4580, from certain minerals. I can see no traces of it in the gas from Bröggerite. A hydrogen line occurs at 4580'1.
4559'4	2	Young gives a chromospheric line at 4558'9.
4544'1	5	
4520'9	3	A faint blue line, seen in "Uraninite, R." Lockyer gives a line at 4522, seen in the gas from some minerals. Young gives a chromospheric line at 4522'9. It is absent in the gas from Bröggerite.
4511'4	5	A blue line, seen in "Uraninite, R." but not in the others. It is coincident with the strong head of a carbon band in the CO ₂ and Cy spectrum.
4497'8	2	There is a hydrogen line at 4498'75.
4471'5	10	A very strong blue line, having a fainter line on each side, forming a close triplet. It is a prominent line in all the samples of gas examined. Young gives the wave-length 4471'8 for a line in the chromosphere, and Lockyer gives 4471 for a line in gas from Bröggerite.
4435'7	9	Seen in "Helium Puriss."
4437'1	1	Young gives a chromospheric line at 4437'2.

* *Journal of the Institution of Electrical Engineers*, Part 91, vol. xx., Inaugural Address by the President, William Crookes, F.R.S., Jan. 15th, 1895.

Wave-length.	Intensity.		Wave-length.	Intensity.	
4428.1	10	{ These two lines form a close pair. I can only see them in "Uraninite, R." No trace of them can be seen in the gases from other sources. Young gives chromospheric lines at 4426.6 and 4425.6.	3890.5	9	{ A very strong triplet, seen in all the samples of gas. Lockyer finds a line having a wave-length 3889 in gas from Bröggerite. Hale gives a chromospheric line at 3888.73. There is a strong hydrogen line at 3889.15.
4424.0	10		3888.5	10	
4399.0	10	A strong line, only seen in "Uraninite, R." Absent in the gas from the other sources. Lockyer gives a line at 4398 in gas from certain minerals. Young gives a chromospheric line at 4398.9.	3885.9	9	
4386.3	6	Seen in all the samples of gas. Young gives a chromospheric line at 4385.4.	3874.6	6	Only seen in "Uraninite, R."
4378.8	8	{ These two lines form a pair seen in "Uraninite, R," but entirely absent in the others.	3867.7	8	Seen in "Helium Puriss."
4371.0	8		3819.4	10	Seen in all the samples of gas. Deslandres gives a chromospheric line at 3819.8.
4348.4	10	Seen in "Uraninite, R." Lockyer finds a line at 4347 in the gas from certain minerals.	3800.6	4	Seen in "Helium Puriss."
4333.9	10	Probably a very close double line. Seen in "Uraninite, R" and "Clèveite, R." Not seen in the other samples. Lockyer gives a line in the gas from certain minerals at 4338.	3732.5	5	Seen in "Helium Puriss." Hale gives a chromospheric line at 3733.3.
4298.7	6	Only seen in "Uraninite, R." Young gives a chromospheric line at 4298.5.	3705.4	6	Seen in all the samples of gas. Deslandres gives a chromospheric line at 3705.9.
4281.3	5	Only seen in "Uraninite, R."	3642.0	8	Only seen in "Uraninite, R."
4271.0	5	Only seen in "Uraninite, R." The strong head of a nitrogen band occurs close to this line.	3633.3	8	Seen in "Helium Puriss."
4258.8	7	Seen in all the samples of gas.	3627.8	5	Only seen in "Uraninite, R."
4227.1	5	Only seen in "Uraninite, R." Young gives a chromospheric line at 4226.89.	3613.7	9	Seen in "Helium Puriss."
4198.6	9	{ These three lines form a prominent group in "Uraninite, R," they are very faint in "Clèveite, R," and in "Bröggerite, L," but are not seen in "Bröggerite, R."	3587.0	5	Seen in "Helium Puriss."
4189.9	9		3447.8	8	Seen in "Helium Puriss."
4181.5	9		3353.8	5	Seen in "Helium Puriss."
4178.1	1	An extremely faint line. Lockyer gives a line at 4177, seen in the gas from certain minerals, and Young gives a chromospheric line at 4179.5.	3247.5	2	Seen in "Helium Puriss."
4169.4	6	Seen in "Helium Puriss."	3187.3	10	The centre line of a close triplet. Very faint in "Clèveite, R," and "Uraninite, R," and strong in "Helium Puriss." and in "Bröggerite, L." It is not seen in "Bröggerite, R."
4157.6	8	A strong line in "Uraninite, R," very faint in "Bröggerite, R," and "L," not seen in "Clèveite, R."	2944.9	8	A prominent line, only seen in "Helium Puriss." and in "Bröggerite, L."
4143.9	7	Strong in "Clèveite, R," in "Helium Puriss.," and in "Bröggerite, L." It is faint in "Uraninite, R," and not seen in "Bröggerite, R." Lockyer gives a line at 4145 in gas from certain minerals.	2536.5	8	Seen in "Helium Puriss." A mercury line occurs at 2536.72.
4121.3	7	Present in all the gases except "Clèveite, R."	2479.1	4	Seen in "Helium Puriss."
4044.3	9	Present in "Uraninite, R," and "Clèveite, R." Absent in the others.	2446.4	2	Seen in "Helium Puriss."
4026.1	10	{ These lines form a very close pair, seen in all the samples of gas, except "Bröggerite, R." Lockyer finds a line in Bröggerite gas at 4026.5.	2419.8	2	Seen in "Helium Puriss."
4024.15	6				
4012.9	7	Seen in all the samples of gas.			
4009.2	7	Seen in "Helium Puriss."			
3964.8	10	The centre line of a dense triplet. Only seen in "Clèveite, R," in "Helium Puriss.," and "Bröggerite, L." Hale gives a chromospheric line at 3964.			
3962.3	4	Seen in all the samples of gas.			
3948.2	10	Very strong in "Uraninite, R," very faint in "Clèveite, R," and not seen in the others. Lockyer finds a line in gas from Bröggerite at 3947. There is an eclipse line at the same wave-length.			
3925.8	2	Seen in "Helium Puriss."			
3917.0	2	Seen in "Helium Puriss."			
3913.2	4	Only seen in "Uraninite, R," and "Helium Puriss." Hale gives a chromospheric line at 3913.5.			

Some of the more refrangible lines may possibly be due to the presence of a carbon compound with the helium. To photograph them a long exposure, extending over several hours, is necessary. The quartz window has to be cemented to the glass with an organic cement, and the long-continued action of the powerful induction current on the organic matter decomposes it, and fills the more refrangible end of the spectrum with lines and bands in which some of the flutings of hydrocarbon, cyanogen, and carbonic anhydride are to be distinguished.

There is a great difference in the relative intensities of the same lines in the gas from different minerals. Besides the case mentioned by Professor Kayser of the yellow and green lines, 5876 and 5016, which vary in strength to such a degree as to render it highly probable that they represent two different elements, I have found many similar cases of lines which are relatively faint or absent in gas from one source and strong in that from another source.

Noticing only the strongest lines which I have called "Intensity 10," "9," or "8," and taking no account of them when present in traces in other minerals, the following appear to be special to the gas from uraninite:—

4735.1
4658.5
4428.1
4424.0
4399.0
4378.8
4371.0
4348.4
4198.6
4189.9
4181.5
4157.6
3948.2
3642.0

The following strong lines are present in all the samples of gas:—

7065.5
6678.1
5876.0
5015.9
4922.6
4713.4
4471.5
4386.3
4258.8
4012.9
3962.3
3890.5
3888.5
3885.9
3819.4
3705.4

The distribution assigned to some of the lines in the above Tables is subject to correction. The intensities are deduced from an examination of photographs, taken with very varied exposures; some having been exposed long to bring out the fainter lines, and some a short time to give details of structure in the stronger lines. Unless all the photographs have been exposed for the same time, there is a liability of the relative intensities of lines in one picture not being the same as those in another picture. Judgment is needed in deciding whether a line is to have an intensity of 7 or 8 assigned to it; and as in the Tables I have not included lines below intensity 8, it might happen that another series of photographs with independent measurements of intensities would in some degree alter the above arrangement.

In the following Table I have given a list of lines which are probably identical with lines observed in the chromosphere and prominences:—

Wave-lengths observed of helium.	Intensities.	Wave-lengths of chromospheric lines,* Rowland's scale.
7065.5	10	7065.5
6678.1	10	6678.3
5876.0	30	5876.0
5015.6	6	5015.9
4922.6	10	4922.3
4870.6	7	4870.4
4847.3	7	4848.7
4805.6	9	4805.25
4713.4	9	4713.4
4559.4	2	4558.9
4520.9	3	4522.9
4471.5	10	4471.8
4437.1	1	4437.2
4428.1	10	4426.6
4424.0	10	4425.6
4399.0	10	4398.9
4386.3	6	4385.4
4298.7	6	4298.5
4227.1	5	4226.89
4178.1	1	4179.5
3964.8	10	3964.0 H.†
3948.2	10	3945.2 H.
3913.2	4	3913.5 H.
3888.5	10	3888.73 H.
3819.4	10	3819.8 D.
3732.5	5	3733.3
3705.4	6	3705.9 D.

* "A Treatise on Astronomical Spectroscopy," by Dr. J. Scheiner, translated by E. B. Frost, Boston, 1894.

† The wave-lengths to which the initials D. and H. are added are wave-lengths of lines photographically detected in the spectrum of the chromosphere by Deslandres (D) and Hale (H). Their photographs do not extend beyond wave-length 3630. Professor Lockyer (*Roy. Soc. Proc.*, vol. lviii., p. 116, May, 1895) has already pointed out fourteen coincidences between the wave-lengths of lines in terrestrial helium and in those observed in the chromosphere, the eclipse lines, and stellar spectra.

NOTE ON HELIUM AND ARGON.

By Prof. H. KAYSER, of Bonn.

HITHERTO helium has been found only in a few minerals, and we do not know as yet in what state it exists there. It may therefore be interesting that I have found it in a free state in Nature. Some time ago I received information that in the springs of Wildbad, in the Black Forest, bubbles of gas rise up which—according to an old analysis of Fehling—contain about 96 per cent of nitrogen. As in all such cases it is possible that considerable quantities of argon may be found, I submitted the gas to analysis. About 430 c.c. were mixed with oxygen, and sparks were caused to strike through it in presence of potassa-lye. The excess of oxygen was then removed by means of potassium pyrogallate. After desiccation there remained 9 c.c., which were filled into Geissler tubes for a spectroscopic examination of the gas. It showed the lines of argon and helium, the latter not in a small quantity, as its lines appeared very bright and could be readily photographed. Runge and Paschen have found that the gas evolved from clèveite and bröggerite is a mixture of two substances, one of which, helium, is most highly represented in the visible spectrum by the yellow line D₃, whilst the other, not as yet named, is represented by the green line $\lambda = 5016 \mu\mu$. Both these elements are also represented in the Wildbad gas, though it seems to me that the second element is here in a smaller proportion than in bröggerite, as the green line is relatively feebler.

In this result it seems to me especially interesting that thus for the first time a place has been discovered where the two gases included under the name "helium" are liberated and stream out into the atmosphere. Hence free helium must be found in the air along with argon. In fact, I have found in Geissler tubes which I had personally filled with the purest argon possible,—and that at a time when I had not yet worked with helium, so that no admixture with it could have occurred in my laboratory,—on direct comparison with helium tubes the presence of D₃ in the argon spectrum; and I have obtained photographically the strong lines at 388.9 $\mu\mu$. The lines are certainly very faint, but I consider the presence of helium in the air of Bonn as beyond any doubt. Whether this presence of gases in the springs of Wildbad has any connection with their hygienic efficacy, and whether the gases occur in similar springs, the future must show.

Bonn, August 10, 1895.

SYSTEMATIC ARRANGEMENT OF THE CHEMICAL ELEMENTS.

By JULIUS THOMSEN.

AFTER D. Mendeleeff and Lothar Meyer, twenty-six years ago, had represented the properties of the chemical elements as a periodic function of the atomic weights, the attempt was made to arrange the elements in a somewhat different manner, so that their periodicity might come to light as completely as possible. The original form which both Mendeleeff and Meyer employed in their tables for the exposition of periodicity contained the elements distributed in groups of seven members (partly, also, of ten members), and the tables contained eleven such groups. But it soon appeared that this division of the entire number of elements did not present the desired periodicity in a fully satisfactory manner, and the tables were modified in such a manner that only the two first groups retained each the number of seven members, whilst the remaining elements were arranged in five groups each of seventeen members, but of these groups only the two first were approximately complete. But this form also had considerable defects; it is especially difficult to find for

			<i>Electropositive Elements.</i>			Cs	133
						Ba	137
						La	138
						Ce	140
						Ne	141
						Pr	144
						—	—
						Sm	150
						—	—
						Gd	156
						Trb	160
						—	—
						Er	166
						—	—
						Thu	171
						Yb	173
						—	—
						—	—
						Ta	183
						W	184
						—	—
						Os	191
						Ir	193
						Pt	195
						Au	197
						Hg	200
						Tl	204
						Pb	207
						Bi	209
						—	—
						—	—

			<i>Electropositive Elements.</i>		
			K	39.85	Rb
			Ca	40.87	Sr
			Sc	44.89	Y
			Ti	48.91	Zr
			V	51.94	Nb
			Cr	52.96	Mo
			Mn	55.	—
			Fe	56.102	Ru
			Co	59.103	Rh
			Ni	59.107	Pd
			Cu	63.108	Ag
			Zn	65.112	Cd
			Ga	69.114	In
			Gr	72.119	Sn
			As	75.120	Sb
			Se	79.125	Te
			Br	80.127	I

H 1	Li	7.23	Na
	Be	9.24	Mg
	B	11.27	Al
	C	12.28	Si
	N	14.31	P
	O	16.32	S
	F	19.35	Cl

Electronegative Elements.

the elements of the numerous rare earths a place suitable to the character of the entire system, since these substances are closely connected, and their atomic weight fall very near together.

The arrangement which I have used, and which is given in the following table, seems to me more satisfactory.

Few words only are needful to explain the significance of this arrangement. Hydrogen, as usual, forms the head of the table. The other elements are divided into three main groups, of which the first contains 2 + 7 elements, the second 2 + 17, and the third 31 elements; after which, then, probably follows a corresponding series of 31 elements, of which, as yet, only two elements are known (thorium and uranium).

The first two groups, each containing two series, quite correspond to the arrangement now customary. But the table shows an essential difference in the collocation of the remaining elements in one series, beginning with

electropositive cesium and concluding with the metals corresponding to the electronegative members, hitherto known only as far as bismuth. A division of the elements of this group into two more classes is not possible if we wish to carry out the character of the entire arrangement according to valence and electrical character.

The table shows in perspicuous manner the relationship of the elements. From hydrogen the lines connecting the kindred elements lead, on the one hand, to the electropositive lithium, and, on the other, to electronegative fluorine, and between these two members the other two members of the first series arrange themselves in the known manner. The members of the second series of the first group connect also in a known manner, each to a kindred member of the first; but in the transit from the second to the third series, i.e., from the first to the second group, the division already observed in hydrogen repeats itself, each member of the second series being related to

the members of the third; that is, with one member belonging to the electropositive part and another belonging to the electronegative part of the third series. Thus, sodium is related to potassium and copper, magnesium to calcium and zinc, aluminium to scandium and gallium, &c., and, lastly, chlorine with manganese and bromine. There then remain three members of the third series (iron, cobalt, and nickel), which form the transition from manganese to copper.

The fourth series connects itself in a known manner to the third, just as in the first group the second series connects itself to the first. On the transition from the second to the third group a similar behaviour takes place as on the transit from the second to the third. Hence, also, the affinity of the elements appears to be demonstrable in two directions; partly in an electropositive and partly in an electronegative direction. Just as we are led from silicon of the first group on the one hand to titanium, and on the other to germanium of the second group, so pass the lines of affinity between the second and third group, e.g., from zirconium on the one hand to cerium with the atomic weight 140, and on the other hand to an element not definitely determined, with an atomic weight of about 181. Between these two elements are grouped a great number of elements corresponding to the rare earths which all display a close relation, as also the intermediate elements of the third series from manganese to zinc.

Many of the elements of the fifth series have only been partially investigated, and their nearest affinities in the fourth series cannot be indicated with certainty; yet we see various analogies among the better known elements. The table gives an indication, by means of dotted lines, such as that of cadmium and ytterbium (known by the peculiar formula of the sulphate).

The atomic weights in the table are carried to the nearest whole numbers, and are merely to serve as guides.

Of the elements of the rare earths, I have included in the table all contained in the table of atomic weights published by F. W. Clarke (*Journ. Amer. Chem. Soc.*, 1894, xvi., 3).

Finally, I wish to draw attention to a curious fact, i.e., that the number of elements in the single series, 1, 7, 17, and 31, may be expressed by $1+2$, $3+2$, $5+2$, 7 . Probably this occurrence of the prime numbers 1, 3, 5, 7, is merely accidental.

Although the table here given differs from the customary tables only in its arrangement, I believe that it presents in a very perspicuous manner the facts which may be deduced from the periodic system.—*Zeitschrift für Anorg. Chemie*, ix., p. 190.

QUANTITATIVE SEPARATION OF METALS IN ALKALINE SOLUTION, BY MEANS OF HYDROGEN PEROXIDE.

By P. JANNASCH and H. KAMMERER.

1. Separation of Manganese and Silver.

For separating these two metals we put into a small beaker 0.7 to 0.8 grm. silver nitrate and an equal quantity of manganese-ammonium sulphate, with 10 c.c. concentrated nitric acid and the same volume of water. The solution is poured into a mixture of 20 c.c. water, 50 hydrogen peroxide, and 40 concentrated ammonia, and the whole is covered and heated upon the water-bath for ten to twelve minutes, whereupon the precipitate of hydrated manganese peroxide, which rapidly deposits, is filtered off. The precipitate is most carefully washed, firstly with a mixture of 8 parts by volume of water, 17 of hydrogen peroxide, and 17 of strong ammonia, and finally with hot water, incinerated, and lastly ignited before the blast until the weight is constant. The filtrate, containing all

the silver, is heated on the water-bath until the ammoniacal odour disappears, acidified with concentrated nitric acid, and the silver is separated as chloride in the ordinary manner.

The separation of manganese and silver proceeds extremely easily and smoothly. A single precipitation of the manganese is perfectly sufficient, as the precipitate on examination was found perfectly free from traces of silver. In more complicated mixtures, e.g., an alloy of silver, bismuth, manganese, and nickel, the new process is decidedly to be preferred to a preliminary precipitation of the silver.

2. Separation of Bismuth and Cobalt.

As our initial material we used cobalt-ammonium sulphate and pure metallic bismuth. About 0.5 grm. of the cobalt salt and 0.35 grm. bismuth are heated in a crucible upon the water-bath with 10 c.c. concentrated nitric acid and 10 c.c. water until dissolved. In a second large porcelain capsule we have in readiness a mixture of 20 c.c. water, 50 hydrogen peroxide, and 50 concentrated ammonia, into which we pour the metallic solution after the addition of 10 c.c. concentrated nitric acid. After subsidence the bismuth precipitate (still including traces of cobalt) is filtered off, and washed first with a mixture of hydrogen peroxide and ammonia, as above, then with dilute ammonia (1:2), and lastly with hot water. When this has been thoroughly done the precipitate is dissolved on the filter with hot dilute nitric acid (1:3), noting the quantity thus consumed, and then add to the cold bismuth solution so much concentrated nitric acid that 20 c.c. of it may again be present in the liquid. The bismuth is then precipitated a second time exactly as before, the precipitate washed precisely as above, dried at 90°, incinerated, and weighed as bismuth oxide in a platinum crucible.

The precipitate, containing all the cobalt, is dried perfectly on the water-bath, and then heated strongly in a large nickel air-bath until all the ammonium salts are expelled. The residual cobalt salt is now taken up with a little hot water, to which a few drops of hydrochloric acid and a little hydrogen peroxide have been added, diluted to at most 100 c.c., and finally precipitated at a boiling heat with a slight excess of pure soda, with the simultaneous addition of some bromine. The precipitate obtained is well washed, dried, incinerated (the filter separately), and weighed as cobalti-cobaltous oxide. Or the cobalt may be directly precipitated from the original ammoniacal solution with ammonium sulphide. This precipitate must be heated for some time on the water-bath until completely deposited, when it is filtered and washed with hot water containing ammonium sulphide. By the use of warm dilute aqua regia alternately with hydrogen peroxide, it is easily practicable to re-dissolve the sulphide for the precipitation of the cobalt with soda and bromine.—*Berichte*, 1895, No. 11, p. 1407.

DETERMINATION OF SMALL QUANTITIES OF ARSENIC.

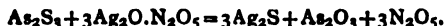
By AD. CARNOT.

We possess already numerous methods for the determination of arsenic; but these procedures, if convenient for large proportions, leave much to be desired in the case of slight quantities. But in a number of instances it is important to determine the latter with accuracy. We know, for instance, that various metals—copper, iron, nickel, &c.—lose in part their industrial value if they contain a proportion of arsenic amounting to one part in a thousand. Great precision is also necessary for the determination of arsenic in mineral waters, where it sometimes plays a most important part, although its proportion scarcely ever attains some tenths of a m.grm. per litre.

The method which I am about to explain consists in precipitating the arsenic in the state of sulphide, transforming the latter into arsenic acid by means of ammonia, silver nitrate, and hydrogen peroxide. The arsenic acid is then determined as bismuth arseniate, a compound very insoluble in dilute nitric acid, the weight of which is nearly five times equal to that of the element to be determined.

The first operation is almost always the necessary complement of the treatment required for isolating the arsenic from other substances. According to the cases, the precipitation of the arsenic is effected either by the action of sulphuretted hydrogen upon an acid solution where it is present as arsenious or arsenic acid, or by the decomposition by means of an acid of a solution in which the arsenic is present as a sulpho-salt. Hence the precipitate is composed of a more or less important quantity of free sulphur.

This mixture, after having been well washed, is treated with hot ammoniacal water; this readily dissolves the arsenic sulphide, leaving on the filter nearly all the free sulphur; the surplus will be precipitated by the following operation:—We pour into the solution a sufficiency of silver nitrate, which produces a precipitate of silver sulphide, and at the same time ammonium arsenite or arseniate, according as the precipitate contained arsenic trisulphide or pentasulphide. For the trisulphide, *e.g.*, the transformation is represented by the following equation:—



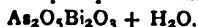
It is heated with stirring for some minutes to collect the precipitated sulphide, and we satisfy ourselves that the liquid is not rendered turbid by a further addition of a silver salt. We then add a few drops of pure hydrogen peroxide (or at least containing no other acid than the hydrochloric), which is without action on silver sulphide, but which, at once, in presence of an excess of ammonia, converts arsenious acid into arsenic acid.

We heat again to near 100°, until the odour of ammonia has totally disappeared, and we add a few drops of nitric acid so as to slightly acidify the liquid. We thus re-dissolve any silver arseniate which has been deposited on the expulsion of the ammonia, and we precipitate in the state of silver chloride all the chlorine which may be derived from an imperfect washing of the arsenic sulphide at the outset, or from an impurity in the hydrogen peroxide employed.

We collect on a filter the precipitates of silver sulphide and chloride, and, after washing, pour into the filtrate a nitric solution of bismuth subnitrate, containing at least five or six times as much of this reagent as there may be arsenic in the substance under analysis.

We saturate with ammonia, and allow to boil for some minutes. The white precipitate of bismuth hydroxide and arseniate is allowed to subside, and the liquor is decanted through a small tared filter. The precipitate on the filter and in the flask is then dissolved by water containing 1/15th of its volume of nitric acid at 1.310, and the solution is caused to boil. This degree of dilution is the most suitable for gradually dissolving the bismuth hydroxide and leaving the arseniate completely insoluble. There is formed a heavy crystalline precipitate, which is collected on the small tared filter, and washed first with water acidulated to 1/3, and then with pure water. It is dried at 110°, and weighed.

The analysis of the precipitate leads to the formula—



It contains, therefore, in 100 parts, 21.067 of arsenic, or 32.303 parts of arsenious acid. The precipitate must be weighed, dried, and not ignited, on account of the losses produced at a red-heat by the reductive action of the paper. A series of experiments prove that this method is very certain and accurate.—*Comptes Rendus*, cxxi., 20.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JULY 31ST, 1895.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, August 12th, 1895.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 189 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from July 1st to July 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 189 samples examined one was recorded as "slightly turbid," and one as "clear, but dull;" the remainder were clear, bright, and well filtered.

July has been the wettest month since November last, when an excess of 2.49 inches of rain fell in the Thames valley. The actual amount of rain during the month just passed was 3.41 inches, and as the mean of 25 years is 2.58 there has fallen an excess of 0.83 inch. With the exception of a heavy storm on the 1st, the first half of July was dry; after the 1st scarcely any rain fell till the 18th, the greater part falling between the 18th and 25th.

The high level of purity of the Thames-derived waters, to which we drew attention in the report for June, was sustained in July, notwithstanding the fact that turbidity and peaty colouring-matters are always washed from the land into a river by heavy rain following a drought. A comparison of the chemical composition of the waters in July and in June shows that the constituents are almost identical in quantity.

We have continued to examine the samples drawn from the clear water wells of the water companies at their works, and from the unfiltered river water. The unfiltered Thames water contained an average of 3425, and the filtered water at the works contained 30 microbes per cubic centimetre.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

THE VOLUMETRIC ESTIMATION OF NICKEL

By THOMAS MOORE.

IN a former number of the *CHEMICAL NEWS* (lix., 160, 293) I described a volumetric method for the now industrially important metal nickel. A great many assays made by this process amply proved its reliability, and in this communication it is proposed to describe a modification by means of which it is rendered one of the most exact processes in analytical chemistry. Those chemists who have employed the original method must have noticed that its weak place lay in the use of cupric ferrocyanide as indicator; this, however, is now dispensed

with, and argentic iodide substituted. The principles upon which the process depends may be thus described:—If to an ammoniacal solution of nickel containing AgI in suspension (argentic iodide being almost insoluble in weak ammonia) there is added potassic cyanide, the solution will remain turbid so long as all the nickel is not converted into the double cyanide of nickel and potassium, the slightest excess of cyanide being indicated by the clearing up of the liquid, and, furthermore, this excess may be exactly determined by adding a solution of silver until the turbidity is reproduced. It is a fortunate circumstance that the complicated side-reactions existing in Parke's copper assay do not appear to take place with nickel solutions, at least not when the temperature is kept below 20° C. This is fully borne out by the fact that the potassic cyanide may be standardised on either silver or nickel solutions with equal exactness. In practice it has been found best to proceed in the following manner:—

Solution of argentic nitrate, containing about 3 grms. of silver per litre. The strength of this solution must be known with as much accuracy as possible.

Potassic iodide, 10 per cent solution.

Potassic cyanide, 22 to 25 grms. per litre. This solution must be tested every few days, owing to its liability to change.

Standardising the Cyanide Solution.

This may be accomplished in two ways: (a) on a solution of nickel of known metallic contents, or (b) on the argentic nitrate solution.

(a). First accurately establish the relation of the cyanide to the silver solution, by running into a beaker glass 3 or 4 c.c. of the former; dilute this with about 150 c.c. of water, render slightly alkaline with ammonia, and then add a few drops of the potassic iodide. Now carefully run in the silver solution until a faint permanent opalescence is produced, which is finally caused to disappear by the further addition of a mere trace of cyanide. The respective volumes of the silver and cyanide solutions are then read off, and the equivalent in cyanide of 1 c.c. silver solution calculated. A solution containing a known quantity of nickel is now required. This must have sufficient free acid present to prevent the formation of any precipitate, on the subsequent addition of ammonia to alkaline reaction; if this is not so, a little ammoniac chloride may be added. A carefully measured quantity of the solution is then taken, containing about 0.1 gm. of nickel, and rendered distinctly alkaline with ammonia, a few drops of potassic iodide added, and the liquid diluted to 150 to 200 c.c. A few drops of the silver solution are now run in, and the solution stirred to produce a uniform turbidity. The solution is now ready to be titrated with the potassic cyanide, which is added slowly and with constant stirring until the precipitate wholly disappears; a few extra drops are added, after which the beaker glass is placed under the argentic nitrate burette, and this solution gently dropped in until a faint permanent turbidity is again visible; this is now finally caused to dissolve by the mere fraction of a drop of the cyanide. A correction must now be applied for the excess of the cyanide added, by noting the amount of silver employed, and working out its value in cyanide from the data already found; this excess must then be deducted, the corrected number of c.c. being then noted as equivalent to the amount of nickel employed.

(b). Having determined the relative value of the potassic cyanide to the argentic nitrate, and knowing accurately the metallic contents of the latter, then $\text{Ag} \times 0.27196$ gives the nickel equivalent. This method is quite as accurate as the direct titration.

A modification of the above process, whereby one burette only is necessary, has been found very convenient, and has given most excellent results. It is based on the following:—When a solution of potassic cyanide, containing a small quantity of argentic cyanide dissolved in

it, is added to an ammoniacal solution of nickel containing potassic iodide, it is seen that argentic iodide is precipitated, and the turbidity thus caused in the solution continues to increase up to the point where the formation of the nickel-potassic cyanide is complete; any further addition after this stage is reached will produce a clearing up of the liquid, until, at last, the addition of a single drop causes the precipitate to vanish. This final disappearance is most distinct, and leaves no room for doubt. Such a solution may be prepared by dissolving 20 to 25 grms. potassic cyanide in a litre of water, adding to this about 0.25 gm. argentic nitrate previously dissolved in a little water. For large quantities of nickel the quantity of silver may advantageously be diminished, and *vice versa*. The value of the cyanide is best ascertained in the manner already described, on a nickel solution.

Small quantities of cobalt do not seriously affect the results, but it must be remembered that it will be estimated along with the nickel; its presence is at once detected by the darkening of the solution. Manganese or copper render the process valueless, so also does zinc; the latter, however, in alkaline pyrophosphate solution exercises no influence. In the presence of alumina, magnesia, or ferric oxide, citric acid, tartaric acid, or pyrophosphate of sodium may be employed to keep them in solution. The action of iron is somewhat deceptive, as the solution, once cleared up, often becomes troubled again on standing for a minute; should this occur, a further addition of cyanide must be given until the liquid is rendered perfectly limpid. The temperature of the solution should never exceed 20° C.; above this the results become irregular. The amount of free ammonia has also a disturbing influence; a large excess hinders or entirely prevents the reaction; the liquid should, therefore, be only slightly but very distinctly alkaline. A word of caution must be given regarding the potassic cyanide, as many of the reputed pure samples are very far from being so. The most hurtful impurity is, however, sulphur, as it gives rise to a darkening of the solution, owing to the formation of the less readily soluble argentic sulphide; to get rid of the sulphur impurity it is necessary to thoroughly agitate the cyanide liquor with oxide of lead, or, what is far more preferable, oxide of bismuth.

As regards the exactness of the methods, it is unnecessary to give an array of figures. This much, however, may be said, that, after a prolonged experience, extending over many thousands of estimations, they have been found to be more accurate and reliable than either the electrolytic or gravimetric methods, and when time is a consideration the superiority is still more pronounced. The employment of organic acids or sodic pyrophosphate in the case when iron, zinc, &c., are present, allows us to dispense with the tedious separation which their presence otherwise entails; and this is a matter of considerable importance in the assay of nickel mattes or German silver.

Nouméa, New Caledonia.

REPORT OF COMMITTEE ON ATOMIC WEIGHTS, PUBLISHED DURING 1894.*

By F. W. CLARKE.

TO THE MEMBERS OF THE AMERICAN CHEMICAL SOCIETY: Your Committee upon Atomic Weights respectfully submits the following report, which summarises the work done in this department of chemistry during 1894. Although the volume of completed determinations is not large, it is known that several important investigations are in progress, from which valuable results may be expected in the near future. It is in this country that the

* From the *Journal of the American Chemical Society*, vol. xvii., No. 3. Read at the Boston Meeting, Dec. 28, 1894.

greatest activity exists, and that the greatest progress is being made at present; and the preparation of these reports is therefore a peculiarly appropriate function of the Society. The data for 1894 are as follows:—

The H : O ratio.—An interesting attempt at the indirect measurement of this ratio, which is the base line upon which our system of atomic weights depends, has been made by Julius Thomsen (*Zeit. Phys. Chem.*, xiii., 398). His determinations are really determinations of the ratio $\text{NH}_3 : \text{HCl}$, and were conducted thus:—First, pure dry gaseous hydrochloric acid was passed into a weighed absorption apparatus containing pure distilled water. After noting the increase in weight, gaseous ammonia was passed through to slight excess, and the apparatus was weighed again. The excess of ammonia was then measured by titration with standard hydrochloric acid. In weighing, the apparatus was tared by another as nearly like it as possible, containing the same amount of water. Three sets of weighings were made, with apparatus of different size, and these Thomsen considers separately, giving the greatest weight to the experiments involving the largest masses of material. The data are as follows,

with the ratio $\frac{\text{HCl}}{\text{NH}_3}$ in the third column.

First Series.		
Wt. HCl.	Wt. NH_3 .	Ratio.
5'1624	2'4120	2'1403
3'9425	1'8409	2'1416
4'6544	2'1739	2'1411
3'9840	1'8609	2'1409
5'3295	2'4898	2'1406
4'2517	1'9863	2'1405
4'8287	2'2550	2'1414
6'4377	3'0068	2'1411
4'1804	1'9528	2'1407
5'0363	2'3523	2'1410
4'6408	2'1685	2'1411
Second Series.		
11'8418	5'5302	2'14130
14'3018	6'6808	2'14073
12'1502	5'6759	2'14067
11'5443	5'3927	2'14073
12'3617	5'7733	2'14118
Third Series.		
19'3455	9'0360	2'14094
19'4578	9'0890	2'14081

From the sums of the weights Thomsen finds the ratio to be 2'14087, or 2'13934 in vacuo. From this, using Ostwald's reduction of Stas's data for the atomic weights of nitrogen and chlorine, he gets the ratio—

$$\text{O} : \text{H} :: 16 : 0.99946,$$

or almost exactly 16 : 1. In a later paper (*Zeit. Phys. Chem.*, xiii., 726), Thomsen himself re-calculated Stas's data, with $\text{O} = 16$ as the basis of computation, and derives from them the subjoined values for the elements which Stas studied:—

Ag	..	..	..	107'9299
Cl	..	..	..	35'4494
Br	..	..	..	79'9510
I	..	..	..	126'8556
S	..	..	..	32'0606
Pb	..	..	..	206'9042
K	..	..	..	39'1507
Na	..	..	..	23'0543
Li	..	..	..	7'0307
N	..	..	..	14'0396

Combining these values for chlorine and nitrogen with his ratio $\text{HCl} : \text{NH}_3$ he gets $\text{O} : \text{H} :: 16 : 0.9992$. This, however, is only an apparent support of Prout's hypothesis, for it depends on the anti-Proutian determinations of Stas. If we calculate from Thomsen's new ratio with

$\text{N} = 14$ and $\text{Cl} = 35.5$, it gives $\text{H} = 1.0242$; which is most unsatisfactory. In short, the method followed by Thomsen is too indirect and subject to too many possibilities of error to entitle it to much weight in fixing so important a constant as the atomic weight of oxygen. The direct processes, followed by several recent investigators, and giving $\text{O} = 15.87$ to 15.89 are much more trustworthy. Meyer and Seubert (*Ber. d. Chem. Ges.*, xxvii., 2770; see also abstract by Ostwald in *Zeit. Phys. Chem.*, xv., 705), in their criticism of Thomsen's work, have pointed out some of its uncertainties.

In this connection it may be noted that Scott's research upon the composition of water by volume, cited by abstract in the report of last year, has been published in full in the *Philosophical Transactions*, 1893, clxxxiv., 543.

STRONTIUM.

The atomic weight of strontium has been re-determined by Richards (*Proc. Amer. Acad.*, 1894, 369) from analyses of the bromide. The first ratio measured, after a careful preliminary study of materials and methods, was that between silver and strontium bromide. Of this ratio, three sets of determinations were made, all volumetric, but with differences of detail in the process. The weights are as follows, with the ratio $\text{Ag}_2 : \text{SrBr}_2 :: 100 : x$ in the third column:—

First Series.		
Wt. Ag.	Wt. SrBr_2 .	Ratio.
1'30755	1'49962	114'689
2'10351	2'41225	114'677
2'23357	2'56153	114'683
5'36840	6'15663	114'683
Sum	11'01303	114'683
Second Series.		
1'30762	1'49962	114'683
2'10322	2'41225	114'693
4'57502	5'24727	114'694
5'36800	6'15663	114'691
Sum	13'35386	114'692
Third Series.		
2'5434	2'9172	114'697
3'3957	3'8946	114'692
3'9607	4'5426	114'692
4'5750	5'2473	114'695
Sum	14'4748	114'694

From these data we have, if $\text{Ag} = 107.93$, and $\text{Br} = 79.955$ ($\text{O} = 16$), the following results:—

From first series	..	..	$\text{Sr} = 87.644$
„ second series	..	..	87.663
„ third series	..	..	87.668

In two additional series, partly identical with the foregoing, the silver bromide thrown down was collected and weighed. I subjoin the weighings with the ratio $2\text{AgBr} : \text{SrBr}_2$ in the last column.

First Series.		
2AgBr.	SrBr_2 .	Ratio.
2'4415	1'6086	65'886
2'8561	1'8817	65'884
6'9337	4'5681	65'883
Sum	12'2313	65'8834
Second Series.		
2'27625	1'49962	65'881
3'66140	2'41225	65'883
3'88776	2'56153	65'887
9'34497	6'15663	65'882
Sum	19'17038	65'883

From the first series .. Sr = 87.660

„ second series... 87.659

The average of all five series is Sr = 87.659.

(To be continued.)

REPORT OF EXPERIMENTS ON THE CHEMISTRY OF THE CYANIDE PROCESS, AND NOTES ON ITS WORKING.

NEW PROCESS FOR DETERMINING CYANIDES.

SOLUBILITY OF GOLD IN DOUBLE CYANIDES AND IN HYDROCHLORIC ACID.

PHENOLPHTHALEIN AS AN INDICATOR IN TITRATING POTASSIUM CYANIDE.*

By G. A. GOYDER, F.C.S.,
Analyst and Assayer to the South Australian School of Mines
and Industries.

(Concluded from p. 82).

ANOTHER method of working the lixiviation process consists in closing the draw-off pipe and filling the vat with water to the top of the filter bed; the tailings are then filled in and levelled, and the strong solution run on. As the air cannot escape below it bubbles up vigorously through the solution, and appears to form channels in the tailings, which result in irregular percolation afterwards; as the solution sinks, more is added from time to time until the vat is full, when a little of the water is drawn off from below, and the solution is then left standing for about twelve hours. The vigorous bubbling which takes place in the vat also causes the mixture of the strong solution with the residual water in the tailings, and thus increases its bulk. The solution displaced by weak liquor is run off at a quicker rate than above, the rest of the process being the same as there described. Judging the two processes by the appearance of the solutions in the syphon bottles, the former process gave a clearer effluent with quicker changes from one solution to the other, and the solution became colourless at the end with less wash water than the latter. As in the latter process the bulk of solution had already been increased at the beginning the quantity of wash water at the end would have to be reduced, or the volume of solution would become unmanageable, and thus gold would be left in the tailings.

The importance of the above, and especially of a thorough washing of the tailings after treatment by cyanide, is emphasized by an instance described by Caldecott, Johannesburg Chem. and Met. Soc., July 28, 1894, in which he says:—"In the re-treatment of a mass of residues by the African Gold Recovery Company, from which on the average 70 per cent of the original gold had already been extracted, the extraordinary fact was discovered that their value was no longer 15 dwts., but 9 dwts. only. Explanations as to the reason of this discrepancy were sought for in vain, until, when all the residues had been re-treated, the site they had occupied was sampled, with the result that the top 3 ins. was found to assay 38 dwts. of fine gold per ton, evidently derived from the soluble gold produced by the cyanide solution contained by the residues continuing to act after discharge, and being washed downward by the rain."

It is evident that the above was due to imperfect washing. Whether the cyanogen compounds left in the tailings had already dissolved the gold when these were thrown out or afterwards dissolved it is quite another question; but I believe the former was more nearly the case than the latter, as assumed by Mr. Caldecott.

The time necessary for the lixiviation of a vat of tailings, &c., varies from twenty-four hours, where the gold is very fine and the solutions pass readily through tailings containing little injurious mineral, to a week or even a fortnight, where the gold is coarser, as in concentrates; but in any case I believe that, where possible, it is advan-

tageous to let the solutions run through slowly and regularly, so that they will all pass in the least time necessary for the best payable extraction, reducing the strength of the solution and increasing its bulk where the gold is coarse, rather than to let the solution stand for some time in the ore and then run it off quickly. In the former case the solution is less liable to form channels, and the rate of flow between the coarse and fine interstices is more even than in the latter case. Also where the solution is always moving fresh cyanide is being constantly brought into contact with the small particles of gold, whereas when the solution is standing all the cyanide near a small particle may soon become exhausted, and fresh cyanide is only able to approach to the attack by the very slow process of diffusion. In the experiments I have made on the small scale the slow even flow gave the best extraction in the least time, and no doubt it would be the same on the working scale.

In the following Table the progress of lixiviation of a vat is shown by analyses of samples drawn from the syphon bottle at intervals of an hour, the solutions being allowed to run continuously, the whole process occupying less than twenty-four hours. The percentages of cyanide given were determined with the addition of excess of caustic soda, as above described, and therefore indicate cyanide of potassium plus cyanide of zinc and potassium plus some other double cyanides formed during the extraction, but not including ferrocyanide of potassium, or mercury, or copper-potassium cyanide. The strong solution used contained 0.3 per cent of potassium cyanide and 0.3 per cent of zinc-potassium cyanide, and the weak solution 0.3 of zinc-potassium cyanide. Both solutions contained between 1 dwts. and 2 dwts. of gold per ton remaining from previous operations.

Analyses of Samples of Solution taken from Syphon-Bottle at Intervals of an Hour during the Lixiviation of a Vat of Tailings.

No. of sample.	Appearance in syphon-bottle.	Percentage of cyanide in sample.	Gold per ton of sample.	Solution run to	
1.. .. .	White	Nil	Nil	Waste water tank.	
2.. .. .	White	0.002	Trace		
3.. .. .	Pale yellow, gradually increasing to full yellow, remaining some time the same tint, gradually decreasing to pale yellow, and becoming very pale.	0.022	0 15	Small zinc boxes.	
4.. .. .		0.056	1 6		
5.. .. .		0.102	8 3		
6.. .. .		0.270	9 2		
7.. .. .		0.370	—		
8.. .. .		0.424	9 18	Large zinc boxes.	
9.. .. .		0.441	10 13		
10.. .. .		0.499	6 12		
11.. .. .		0.540	—		
12.. .. .		0.550	4 20		
13.. .. .		0.500	—		
14.. .. .		0.404	2 14	Small zinc boxes.	
15.. .. .		0.302	—		
16.. .. .		0.228	2 6		
17.. .. .		0.200	—		
18.. .. .		0.180	2 14		
19.. .. .		0.150	—		
20.. .. .		0.095	2 6		
21.. .. .		0.061	1 15		
Left draining..		—	—	—	

It will be noticed that the solutions do not pass as rapidly from one to the other as they should do. This is in consequence of the bottoms of the vats not sloping towards the draw-off pipe, and causing a mixture of the solutions in the vats. Had the vats been properly constructed in this respect I believe the water, at the commencement, could have been run off for another hour or more before the gold appeared, and similarly at the end of the process No. 16 to 18 should have shown 0.3 per cent cyanides, and the percentages then run down rapidly until not more than 0.005 should be contained in the twenty-first hour,

while the gold in the same sample should not be more than a trace. It is also very evident that had the first two hours' running been added to the zinc boxes in addition to another hour's running of water at full speed, not included in the table, the same amount would have been left in at the end, and that all the gold indicated from 18 to 21 would thus have been left in the tailings in solution, or the bulk of solution duly increased.

The next Table, which gives the result of a laboratory experiment, is not strictly comparable to the last one, as the ore was dry at the start and had not had the coarse gold removed by the battery. The bottom of the apparatus, however, sloped properly to the draw-off pipe, and it will be noticed how rapidly the strength of the solution, both in cyanide and gold, decreases after No. 15, when the wash-water began to appear, and on the large scale I believe it would decrease even more rapidly than this. The percentage of cyanide in the solutions was determined by the ordinary process, without the addition of caustic alkali. It will be noticed that the solutions contain rather more gold after standing than before, but much of the gold in this stone was much coarser than would obtain in an ordinary tailings, and a larger excess of cyanide was present than would be the case on the working scale; 3000 c.c. of cyanide solution, 0.2 per cent, was gradually poured on the ore, and was collected in lots of 200 c.c. for analysis.

Analysis of Solutions running from Experimental Percolator during the Lixiviation of a Rich Sample containing Coarse Gold.

200 c.c.	Per cent of cyanide in sample.	Gold per ton in sample.			Remarks.
		Ozs.	Dwts.	Grs.	
1.. ..	0.044	4	9	0	
2.. ..	0.103	5	16	0	
3.. ..	0.147	4	10	0	
4.. ..	0.165	3	1	0	Stopped and left standing 17 hours.
5.. ..	0.158	3	11	0	
6.. ..	0.180	2	6	0	Stopped for 46 hours.
7.. ..	0.154	2	20	0	
8.. ..	0.172	2	12	0	
9.. ..	0.172	1	8	0	
10.. ..	0.172	0	19	0	Stopped for 18 hours, and wash-water added.
11.. ..	0.145	0	12	0	
12.. ..	0.154	0	6	12	
13.. ..	0.176	0	4	21	
14.. ..	0.165	0	4	21	
15.. ..	0.091	0	3	20	Wash-water begins to show.
16.. ..	0.015	0	0	18	Cyanide solution nearly all gone.
17.. ..	0.005	trace			

Some experiments were made at Mount Torrens to determine whether by allowing each lot of solution added to the tailings to drain away before adding more solution, and so causing the air to penetrate the tailings intermittently with the solution, a more perfect extraction could be attained. As, however, the results were no better than by the usual method, and as unnecessary aeration promotes loss of cyanide, it appears better to add the solutions until the last wash water has been added as soon as the previous lot has sunk to the surface of the tailings.

A sample of concentrates, mostly pyrites, received here for testing as to its suitability for treatment by the cyanide process, was found by a preliminary washing to contain so much ferrous sulphate as to decompose cyanide of potassium at the rate of about 150 lbs. per ton of con-

centrates. After washing, however, 67 per cent of its gold contents were extracted without undue consumption of cyanide. In last year's report I alluded to the Eureka ore as requiring too much cyanide to be profitably treated by that process. The basic salts in this ore are not readily removed by washing; but when the ore is passed through the battery these salts are so effectually removed as to make the tailings readily amenable to treatment by cyanide. A sample analysed by me contained about $\frac{1}{2}$ per cent of copper. W. R. Feldtmann (*loc. cit.*) recommends that where tailings require a preliminary wash before treatment by cyanide, that the washing should be done in a separate vat reserved for that process only, as "when a water wash charged with acid out of the ore comes in contact with residual quantities of cyanide solution lying in the bottom and adhering to the sides of the tank, a certain quantity of hydrocyanic acid gas is liberated, which, diffusing through the whole tank, is capable of dissolving a not inconsiderable amount of gold from the ore; such dissolved gold is not precipitated even if passed through zinc, and is consequently run to waste with the water wash." In this explanation Mr. Feldtmann appears to assume that the solvent action of hydrocyanic acid on gold is at least equal to that of cyanide of potassium. As I have seen no records of experiments on this point I have just made one, placing a gold leaf in a bottle and adding 50 c.c. of 1 per cent cyanide of potassium, to which an equivalent of hydrochloric acid had just been added to set free the hydrocyanic acid: after being left in the bottom for four days, with occasional violent shaking, the solution was filtered off from the undissolved gold, and the gold dissolved was found to amount to 65 per cent of the whole taken. The solvent action of hydrocyanic acid on gold in the presence of air is therefore decided, but very slow. A solution of cyanide of potassium of 0.1 per cent would have dissolved the whole of the gold leaf under similar circumstances in about five minutes.

Judging, however, from the complete removal of soluble salts from the Eureka ore in passing through the battery, it appears to me that with a sample of tailings containing deleterious soluble salts, and not requiring to go through the battery, these salts could be most effectually removed by passing the tailings over a shaking table, using plenty of water.

The large quantity of cyanide of potassium decomposed by ferrous and other soluble metallic salts points to the advisability of transferring the tailings, and especially those containing pyrites, from the pits to the vats with as little exposure to damp air as possible, and also of testing the water running from the vats before the addition of cyanide to ascertain whether a preliminary wash is required.

In order to ascertain whether the gold left in the tailings after treatment by cyanide could be extracted by further treatment, I procured from Mr. L. W. Grayson a sample from the tailings heap at Mount Torrens, and treated a portion of it with excess of $\frac{1}{2}$ per cent cyanide of potassium by continuous percolation for forty-eight hours, thoroughly washing out the cyanide at the end. The tailings before treatment contained gold at the rate of 1 dwt. 13 grs. per ton, of which 8 grs. were extracted by the above treatment. The same sample was again treated in a similar manner by fresh solution, but only yielded $\frac{1}{2}$ gr. per ton. The same sample was then treated with a large excess of strong bromine water during three days, percolating during the day and stopping with the percolator full during the night. During this treatment the small quantity of pyrites present was oxidised, but no gold was dissolved.

The sample was then removed from the percolator, dried, and separated by sieves into three grades, which were assayed separately with the following result—the number of the sieves represent holes per linear inch:—Two per cent, retained by 30-sieve, assayed 8 dwts. 3 grs. of gold per ton; 29 per cent, retained by 60-sieve, as-

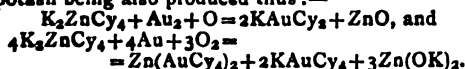
assayed 2 dwts. 7 grs. of gold per ton; 69 per cent, which passed 60-sieve, assayed 14 grs. of gold per ton, from which it was calculated that the gold would be divided as follows in a ton of the tailings:—Three grains of gold would be contained in 45 lbs. of coarse tailings; 17 grs. of gold would be contained in 650 lbs. of medium tailings; 11 grs. of gold would be contained in 1545 lbs. of fine tailings.

Another sample treated in a similar manner yielded:—20·6 per cent, retained by 40-sieve, assayed 3 dwts. 7 grs. of gold per ton; 12·0 per cent, retained by 60-sieve, assayed 2 dwts. of gold per ton; 67·4 per cent, that passed 60-sieve, assayed 1 dwt. 4 grs. of gold per ton. Therefore, 16 grs. of gold would be contained in 460 lbs. of coarse tailings; 5 grs. of gold would be contained in 270 lbs. of medium tailings; 18 grs. of gold would be contained in 1510 lbs. of fine tailings.

Another sample of tailings which had been treated by cyanide contained 3 dwts. of gold per ton, and yielded 1 dwt. to further treatment as above by cyanide, and the gold remaining was equally distributed in the coarser and finer portions.

It would therefore appear that this residual gold cannot be extracted by solvents without further comminution of the tailings, and must therefore be surrounded by matrix impermeable to the solutions. It is further evident that in the above-cited cases the tailings could hardly pay the cost of concentration, re-crushing, &c., necessary to extract some of the balance of the gold.

During my stay at Mount Torrens in April, I inferred from the method in which the cyanide process worked that the double cyanide salts present in the sump liquors must have a considerable solvent action on gold, and found on testing some of these sump liquors that they dissolved gold leaf at about a third of the rate of alkaline cyanide. After my return, therefore, I prepared some of these double cyanides and purified them by crystallisation, several times repeated, and found that zinc potassium cyanide dissolved gold in the presence of oxygen with the production of gold potassium cyanide and oxide of zinc; part of the cyanide also appeared to be transformed into aurocyanide of potassium and auricyanide of zinc, zincate of potash being also produced thus:—



The cyanide of copper and potassium reacted in a similar manner, but somewhat more slowly.

The double cyanide of mercury and potassium does not appear to dissolve gold, even after four months' contact, with occasional shaking. This experiment, however, is not yet finished.

I have not yet tested the double cyanide of calcium and potassium, which may be present in sump liquors from double decomposition, but probably it would be a better solvent for gold than the zinc double salt.

According to W. R. Feldtmann (*Engineer and Mining Journal*, lviii., 1894, 218, 219) the African Gold Recovery Company have made some experiments recently, showing that zinc potassium cyanide has a solvent action on gold in its ores and in the absence of any free potassium cyanide.

I have not yet had time to investigate the nature of the double salts formed in the lixiviation process apart from those formed in the zinc boxes, but believe there must be some double salt (or salts) formed which is more active as a solvent for gold than the double zinc salt. Possibly it may be the double iron salt, K_2FeCy_4 , but this is quickly converted by excess of cyanide of potassium into ferrocyanide of potassium, which I find takes months to dissolve gold leaf. I have not had time to determine the reactions involved.

To the solvent action of these double salts on gold, especially on ores containing copper or other "refractory" minerals, the success of the cyanide process is without doubt to a large extent to be attributed.

NOTICES OF BOOKS.

The Chemistry of Urine. A Practical Guide to the Analytical Examination of Diabetic, Albuminous, and Gouty Urine. By ALFRED H. ALLEN, F.I.C., F.C.S., Past President of the Society of Public Analysts, &c. 8vo., pp. 212. London: J. and A. Churchill. 1895.

THE author of this manual tells us that he has been led to take up thoroughly the chemical examination of urine, with especial reference to the requirements of physicians called on to act as referees for Life Assurance Companies as well as in questions of diagnosis and prognosis. Hence Mr. Allen has given special attention to the examination of diabetic, albuminiferous, and gouty urines. It has not been his object to produce a complete manual of urinary analysis.

The various methods for the scrutiny of urines are critically examined, and the conditions of their trustworthiness or fallibility are carefully expounded. Hence the book will be of sterling value not merely to physicians, but also to analysts, especially such as have not made this department of chemistry a leading study.

The Consistence-Meter, German Patent, No. 81,265. (Der Consistenz-Messer, D.R.P. 81,265). Berlin: Bernhard Paul.

THIS pamphlet is in substance the very voluminous specification of a German patent. The author, Dr. Weiss, has devised an instrument by which the amount of solids contained in an extract, solution, &c., is estimated by the sinking of a suspended disc. The procedure is applied to fatty oils, solutions of gums, sugars, milks, beers, to the determination of starch in grain, in potatoes, seed-cakes, &c.

The general question arises, whether patents for any analytical or other scientific appliance are not objectionable on the same principle as is a patent for an analytical procedure.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxi., No. 4, July 22, 1895.

Osmotic Phenomena produced between Ether and Ethylic Alcohol, through different Diaphragms.—F. M. Raoult.—The author's experiments prove that the osmose between two given liquids may not merely vary greatly in energy, but even change its direction with the nature of the diaphragm, and that the osmotic movement of substances through the diaphragm may be absolutely independent of their molecular weight and of their function as dissolved bodies or as solvents.

Action of Phenyl Isocyanate upon certain Acids and Ethers.—A. Haller.—Not suitable for useful abstraction.

On Crystalline Anhydrous Manganese Hydrate.—A. Bourlot.—This paper will be inserted in full.

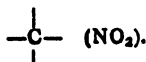
Certain Properties of Compounds of Ferrous Chloride and Nitric Oxide.—V. Thomas.—The author seeks to ascertain whether the compounds which he has recently obtained (*Comptes Rendus*, Feb. 28th and July 8th, 1895) are or are not dissociable. He concludes from his experiments that none of the three compounds described has a tension of dissociation appreciable at the ordinary temperature. There is a very decided difference between the

compounds obtained by M. Gay in the state of solution and those which the author has obtained by the dry way.

On some Alkaline Phosphides.—C. Hugot.—The two phosphides P_2K and P_3K , the preparation of which he describes, are decomposed by moist air with disengagement of hydrogen phosphide. If an excess of ammonium is caused to act upon red phosphorus we obtain new compounds which the author is studying.

Specific Heats of Superfused Formic and Acetic Acids. Modifications to be introduced into Regnault's Thermo-calorimeter for the Determination of the Specific Heats of a great number of Superfused Liquids.—MM. Massol and Guillot.—The specific heats in the solid state are much higher than the specific heats in the liquid state. The specific heat in the liquid state decreases with the temperature. In the state of superfusion the specific heat augments slightly.

Synthetic Formation of Mixed Alcohols.—Louis Henry.—The reaction capacity of methanal with nitromethane, nitro-ethane, and nitro-isopropane corresponds to the number of hydrogen atoms enclosed in the carbonic system.



Oxidation of Inactive Campholenic Acid.—A. Behal.—Not suitable for abridgment.

Constitution of Vegetable Albumenoid Substances.—E. Fleurent.—The failure of the proportion—

$$\frac{N \text{ determined}}{N \text{ calculated}} = 1$$

is due to the presence in gluten, caseine, and vegetable fibrine of a glutamine group, and in legumine and vegetable albumen of an asparagine group.

No. 5, July 29, 1895.

Action of Aniline upon Mercurous Iodide.—Maurice François.—The decomposition of mercurous iodide by aniline is limited, and it is the same with the combination of mercuric iodide and mercury in presence of aniline. The author finds that when a state of equilibrium is reached the liquid always contains, at the boiling-point of aniline (182°), 26.35 grms. mercuric iodide in 100 grms. of the mixture. The action of aniline upon mercurous iodide is comparable to the action of water upon bismuth nitrate, mercuric sulphate, &c., studied by M. Ditte, and follows analogous laws.

Action of Hyponitric Anhydride upon Campholenic Acid.—MM. A. Béhal and Blaise.—If we fix a mol. of NO_2 , and treat the blue liquid with a saturated solution of potassium bicarbonate, there remains a blue insoluble oil, which soon solidifies. When re-crystallised from alcohol at 80° it forms slender blue laminae, fusible at 134.5 , having the composition $C_{10}H_{15}NO_3$. It is neutral, does not decompose alkaline bicarbonates, and may be obtained in two modifications, which may be named ceruleonitrosocampholenolide and leuconitrosocampholenolide.

The Condensation-Products of Isovaleric Aldehyde.—L. Kohn.—The author has obtained two products; the one, boiling at 82° under a pressure of 15 m.m., seems identical with that studied by Kekulé, Fittig, Beilstein, and others, and probably with the product obtained by Barbier and Bouveault. The second product is an oil of feeble odour, colourless, boiling at 140° under a pressure of 18 m.m. It seems to be a polymer of valerol.

The Determination of Boric Acid.—MM. H. Jay and Dupasquier.—This paper will be inserted in full.

Revue Universelle des Mines et de la Metallurgie.
Vol. xxx., No. 2.

This issue contains no chemical matter.

MISCELLANEOUS.

Responsibilities of Manufacturers in Germany.—The following remarkable decisions against employers have been lately given by the "Reichsversicherungsamt":—*a.* The death of a workman in consequence of drinking, at the Works, out of a bottle containing hydrochloric acid, in mistake for a bottle of "schnaps" which the deceased had brought with him. *b.* Malicious poisoning by a fellow-workman, on the pretext that the quarrel was due to a disagreement over work. *c.* Injuries from the explosion of a dynamite cartridge which workmen on strike had left on the premises with criminal intent. *d.* A workman was overwhelmed with stones, &c., in a quarry; a fellow-workman, suffering from palpitation, was so excited that he died. *e.* In order to cure an injury to the fingers, received whilst at work, a labourer was sent by his employers to a medical institute at Hamburg. Whilst there (in autumn, 1892) he died of cholera, and his death was decided to be a working disaster. (Which of these decisions is the most signally inequitable might be the subject of a prolonged discussion.)—*Chemiker Zeitung.*

On Periodical Fluctuations of the Intensity of the Earth's Gravity, and their Influence on Determinations of Atomic Weights.—Dr. G. Paul Drossbach.—If a metallic cone with a very obtuse optical angle is brought in contact with a mercurial horizon, the slightest fluctuations of the level of this cone must present the most different resistances conceivable to a quantity current. For the experiment the cone is suspended to a metal spring. The resistance varies from morning to evening, all accessory causes being of course taken into account. The difference of gravitation was compensated by the addition of weights and thus directly determined. The difference between morning and evening seems to be 0.008 grm. per 100 grms. This indicates a speed of the movement of gravity of about 380 to 400 m.m. The difference between midnight and noon seems to be rather greater, so that the maximum effect of gravitation falls at midnight and morning.—*Chemiker Zeitung.*

DEPARTMENT OF SCIENCE AND ART.

ROYAL COLLEGE OF SCIENCE, DUBLIN.

Required a Demonstrator of Chemistry and Assaying.—For particulars apply to SECRETARY, Royal College of Science, Dublin.

HARRIS INSTITUTE, PRESTON.

Wanted, an Assistant to the Professor of Chemistry. A practical knowledge required of General and Agricultural Chemistry, with some experience in Analytical work. Salary, £100 a year. Applications, stating qualifications, and accompanied by copies of three testimonials, to be forwarded before the 1st of September, 1895, to—

T. R. JOLLY, Secretary.

NOTICE.

The STUDENTS' NUMBER of the CHEMICAL NEWS will be published on Friday, September 6th. Gentlemen holding official positions in the Universities, Medical Schools, &c., of the United Kingdom, where Chemistry and Physical Science form a part of the education, who have not yet forwarded the necessary information to our Office for publication in that Number, will confer a favour by sending it with the least possible delay.

Advertisements for this Number should reach the Office not later than Wednesday, the 4th Sept.

THE CHEMICAL NEWS.

VOL. LXXII., No. 1866.

THE SPECTRUM OF RAMSAY'S COMPOUND OF ARGON AND CARBON.

By WILLIAM CROOKES, F.R.S., &c.

IN the CHEMICAL NEWS for the 2nd of August last (vol. lxxii., p. 51) Professor Ramsay announced the probable existence of a compound of argon and carbon formed by an electric arc between purified carbon poles in an atmosphere of argon. Professor Ramsay kindly filled a quartz-ended tube for me with the resulting gas at the requisite degree of exhaustion for the greatest luminosity, and I have taken several observations on its spectrum, both by the eye and photographically.

The eye observations show an extremely luminous spectrum, in which many of the stronger lines of argon are visible. Measurements were taken of the following argon lines:—

7646	5909	5185.8
7506	5887	5165
7058	5834	4879
6965.6	5803	4509.5
6664	5771	4335
6407	5651	4272
6173	5610	4259.5
6045	5557	4201
6038	5496.5	4159.5

On comparing these with the extended table of the argon spectrum given in the CHEMICAL NEWS for August 9th, it will be seen that they include all the strongest lines in the visible spectrum. Others, less intense, would probably have been seen had not the luminosity of the continuous spectrum interfered with vision.

Examination of the photographs show that in the ultra-violet portion of the spectrum there are also many argon lines, but a little above wave-length 3400 the strong lines due to water-vapour interfere too much to allow the argon lines to be detected.

The higher portions of the visible spectrum show finely channelled groups. These are very prominent in the photographs, and on superposing them on photographs of benzene vapour, carbonic anhydride, and cyanogen, taken under identical conditions, it is seen that the channelled bands are due to a carbon compound, the argon-carbon bands being identical with some of those of cyanogen and carbonic anhydride, and not so strong.

I have looked in vain for lines which are not in the argon, carbon, or water-vapour spectra, and have not found any.

The spectrum of water-vapour is due to moisture, the gas not having been perfectly dried before it was sealed in the tube.

The argon lines are probably caused by excess of argon mixed with the argon-carbon compound, the mode of formation making it very unlikely that all the argon had united with carbon.

Professor Ramsay informed me that the nitrogen had all been removed from the argon before it was submitted to the action of the arc, and special precautions were also taken to remove occluded gases from the carbon-poles.

The coincidence of some of the bands of the new compound with those of cyanogen must not be used as an argument in favour of the theory that argon is a condensed form of nitrogen. Most volatile compounds of carbon have very similar spectra. If photographs of the spectra of carbonic anhydride, carbonic oxide, benzene-vapour,

cyanogen, &c., are superposed, there will not only be seen a general resemblance between them, but in many of the systems of fluted bands there is absolute identity. All that can be said, therefore, is that the compound of argon and carbon gives a similar spectrum to that of most carbon compounds.

I have looked in vain for any line of helium in this spectrum.

London, August 14, 1895.

THE BLUE SPECTRUM OF ARGON.

By Prof. H. KAYSER.

IN the following Table I give a preliminary list of the wave-lengths of the lines of the blue argon-spectrum between $\lambda=340 \mu$ and $\lambda=520 \mu$.

The gas was prepared from atmospheric air, first by copper and magnesium, then by sparking in the presence of caustic potash and absorbing the oxygen by pyrogallic acid and caustic potash. Finally, the gas was dried by phosphorus pentoxide. At different times small quantities of argon were thus prepared, and many Geissler tubes filled at a pressure of 2.2 m.m., which seemed to give the best results. With a Leyden jar and air break a beautiful blue light is produced. The spectrum was photographed with a large Rowland concave grating of 21 feet radius. The different tubes all gave the same lines, only one tube showed the hydrogen lines, and in another appeared the strongest lines of the red argon spectrum. I have photographed also the red spectrum, which appears without a Leyden jar, but have not yet finished the measurement and calculation of the plates. The two spectra have no lines in common, as far as I see.

For the calculation of the wave-lengths in every case the spark spectrum of iron was photographed at the same time on the plates, so that no shifting of the two spectra could occur. For the wave-lengths of the iron lines Rowland's standards were taken.

The numbers in the Table are means of 3 to 6 independent measures; the stronger lines may have an error amounting to 0.001 μ , but the weaker ones are less accurate, and it is not impossible that in a few cases there may be an error of 0.01 μ . 10 signifies the greatest intensity, 1 the weakest. The lines of the blue argon spectrum do not appear among the Fraunhofer lines, as appears from a comparison with Rowland's publications on the lines of the solar spectrum.

I shall soon add the red, yellow, and the remaining ultra-violet part of the blue spectrum, and also the red one; then I shall also discuss these spectra for series. I wish only to state yet, that the red argon line at 706.7 μ is not coincident with the red helium line at 706.5 μ , but has a greater wave-length.

3454.291	2	3521.428	2
3464.387	2	3522.098	1
3466.333	2	3535.517	3
3476.921	5	3545.778	5
3478.385	1	3546.016	5
3480.643	5	3548.705	2
3491.019	1	3559.707	8
3491.420	5	3561.218	7
3491.705	7	3565.223	2
3499.812	3	3576.810	8
3502.342	2	3581.804	4
3503.715	2	3582.550	7
3509.475	3	3588.634	9
3509.962	3	3592.231	1
3511.284	8	3606.072	2
3511.790	1	3622.362	2
3514.354	4	3638.025	7
3514.561	4	3640.024	2
3517.942	1	3651.132	1
3520.179	3	3655.465	3

3656.264	1	4089.041	1
3660.636	1	4104.102	7
3669.632	1	4112.915	1
3678.476	2	4131.919	4
3680.075	1	4146.761	1
3692.736	1	4156.293	2
3712.963	1	4178.477	1
3716.667	1	4179.478	1
3717.316	1	4183.109	2
3718.393	3	4199.226	1
3720.609	1	4202.115	2
3724.563	1	4203.592	1
3729.464	9	4218.867	3
3738.084	3	4222.848	3
3750.294	1	4227.142	2
3753.768	1	4228.301	5
3756.529	1	4229.059	1
3763.718	3	4229.874	1
3765.461	5	4237.397	3
3766.317	2	4266.385	6
3770.721	2	4275.330	1
3776.885	1	4277.720	6
3781.022	6	4283.084	3
3786.558	2	4298.215	1
3795.512	3	4300.817	2
3799.615	2	4309.317	2
3800.429	1	4331.359	6
3803.383	2	4332.205	3
3808.754	1	4333.701	2
3809.645	3	4335.471	1
3825.831	1	4337.258	1
3826.983	3	4343.912	2
3830.603	1	4345.330	1
3841.706	1	4348.231	10
3844.905	1	4352.374	4
3845.536	1	4362.240	2
3850.721	8	4367.963	1
3858.467	2	4370.921	4
3868.700	6	4371.504	4
3872.345	2	4375.266	1
3874.288	1	4376.129	3
3875.413	3	4379.832	6
3880.432	1	4383.900	2
3891.547	2	4400.269	3
3892.118	4	4401.165	5
3900.750	1	4408.102	1
3907.896	1	4421.102	1
3911.678	1	4426.170	9
3914.918	3	4430.365	6
3925.897	3	4431.176	4
3928.750	7	4434.010	2
3931.348	1	4439.541	1
3932.705	4	4443.545	1
3937.208	1	4449.128	2
3944.412	4	4460.683	2
3946.275	3	4475.035	2
3952.868	1	4482.000	5
3960.620	2	4498.874	1
3968.499	3	4503.099	1
3974.662	1	4545.231	5
3979.517	3	4579.531	5
3992.208	2	4589.087	5
4013.997	6	4609.750	6
4023.730	1	4658.070	4
4034.019	2	4727.032	4
4035.630	2	4736.069	5
4038.968	2	4765.030	3
4043.047	4	4806.185	6
4053.118	1	4847.965	3
4072.158	7	4897.997	4
4072.587	3	4965.234	2
4076.869	2	5009.615	2
4077.207	2	5017.421	1
4079.732	2	5062.258	2
4080.850	1	5145.659	2
4082.553	1		

Bonn, July 12, 1895.

ON THE PRODUCTION OF CITRIC ACID
FROM CANE-SUGAR.

(SECOND NOTE).

By Dr. T. L. PHIPSON.

WHEN I published my recent note on this subject I should have remarked that Prof. Maumené (*Comptes Rendus*, April 8, 1895) had already obtained two new organic acids by the action of permanganic acid on cane-sugar; and that Liebig formerly announced that he had obtained tartaric acid by the action of dilute nitric acid on sugar.

I have found that in the grape, the apple, &c., these acids disappear as the sugar is formed, from the outside to the inside of the fruit, and that the remaining acid is concentrated around the seed, probably acting as an antiseptic until germination ensues. It is thus evident that organic acids are formed in fruits before the sugar is formed, and that the sugar may possibly be derived from them. Nevertheless, the ease with which sugar is converted into carbonic acid, formic acid, oxalic acid, &c., and its original production from the starch of the seed during germination, points to the possibility of all other organic acids devoid of nitrogen being obtainable from sugar.

In treating cane-sugar in the cold with permanganic acid as described in my first note, I obtained an acid having some resemblance to citric acid, but no sufficient quantity was obtained to prove its real nature, and I have since been unable to repeat this experiment, but hope to do so shortly. I found, however, that other acids are liable to be formed at the same time, according to the degree to which oxidation is allowed to proceed.

Some chemists who have repeated my first experiment have only succeeded in obtaining sulphate of lime. Probably they used too much sulphuric acid, and did not separate the organic acid by alcohol as I did.

The Casa Mia Laboratory, Putney,
London, August 20, 1895.

SEPARATION OF GOLD AND SILVER FROM
IRON AND STEEL.

By H. N. WARREN, Research Analyst.

To make an accurate and complete analysis of either iron or steel, as is well known, frequently requires a considerable quantity of the sample under examination to become dissolved or otherwise acted upon, in order to ascertain the various constituents present, which are otherwise rendered latent by the large excess of iron associating them. But cases are few and far between where 4 lbs. in weight have to be operated upon, as was the case last week at the Research Laboratory, when an extraordinary examination was required in order to ascertain the relative amounts of both gold and silver present. For examination and estimation of silver 4 lbs. in weight of each sample were selected, the product being bar iron of one inch circumference; each bar was attached to the positive of a battery of 3 volts 40 ampères, whilst a carbon electrode furnished the negative, dilute vitriol being employed as the solvent. Dissolution was completed in forty-eight hours, save a thin wire of iron, which was allowed to remain in order to ensure retention of the silver present in the carboniferous residue.

The residue was next dried and intimately mixed with an excess of chemically pure litharge and reduced in the usual way. The silver separated by cupellation, and gold by parting.

Of the four samples thus treated, the silver, being estimated as percentage of the carboniferous residue, amounted to as follows:—Iron of Swedish origin, 0.8; silver from Shortridge and Howell, 0.055; Low Moor iron,

0.100; Dannemora, 0.064; in each case traces of gold were obtained by parting.

Bars of steel similarly treated yielded percentages approximating 0.078, 0.043, 0.098, 0.032.

Liverpool Research Laboratory,
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GRADATION IN PRESSURES.

By Dr. L. C. LEVOIR.

THE principle of gradation in pressures, utilised in so prolific a manner by Cailletet, in condensing such gases as oxygen and hydrogen, is useful in organic chemistry for saving the life of sealed tubes and valuable preparations.

"Krakatoog" was the term which my students used when in the Bomb Room sealed tubes in the apparatus of Carius, &c., fell to ruin. Bursting can easily be prevented by heating the sealed tube by means of a coil glowing by electricity. The conductor passes through isolated plugs hermetically sealed in inward conical tubes. By a hydraulic pump the pressure outside of the sealed tube is increased. I used a series of ends of boiler tubes, and they worked as a vault or arch to charge or burden the breakable tube outside. In this way, in five successive small boilers, and the coiled tube in a vessel of earthenware without bottom, rolled in vulcanised indiarubber cloth, I have saved the lives of many tubes. I heated water saturated at 0° with hydrochloric acid to 250° without loss.

Ryswick, near The Hague,
August 10, 1895.

A REFORM IN CHEMICAL, PHYSICAL, AND TECHNICAL CALCULATIONS.

By C. J. HANSSEN, C.E.

(Continued from p. 9).

Evaporation of Water (Steam).

If water is heated in a hermetically closed vessel, the steam produced is under the condition "constant

volume." In the working of steam boilers, this is only the case while a boiler is started or "fired up," or during interruptions of the working; in boilers in regular work the steam flows out as fast as it is produced, and the quantity of water in the boiler and the quantity of heat stored up in the water remain unaltered, although new water is fed into the boiler to make up for the water passing off as steam.

The quantity of heat required to evaporate 1 kg. of water, and which passes away with that 1 kg. of steam, has only passed from the fire *through* the water stored up in the boiler; and to find the quantity of heat theoretically required to produce 1 kg. of steam, of any desired density, we have only to ascertain how much heat that 1 kg. of steam is able to contain. The specific heat of water at various temperatures has no influence in the question, and has only to be considered if we were to ascertain the exact quantity of heat required to "fire up" a boiler.

In a boiler in regular working the condition is "evaporation at constant pressure," just the same as evaporation in an open vessel would be if the atmosphere of our globe had the pressure or density existing in the steam boiler; and the temperature of saturated steam in a boiler is equal to the temperature at which water would boil in an open vessel, in an atmosphere equal in density to that in the boiler.

Although steam, for practical purposes, is generated by the evaporation of water, it is useful for the investigation of its properties to consider the production of steam by combination of hydrogen and oxygen, which enables us, in a very simple way and more accurate than by experiment, to find volume, weight, pressure, and other properties of steam, due to any temperature, &c.

In the former chapters it is shown that 1 cbm. steam of atmospheric density and 273° N. absolute temperature (0° N.), formed of combined H and O, must weigh 45/56 kg., that 1 kg. of similar steam is = 56/45 cbm. in volume, and that heated to 373° N. absolute (+100° N.), the proper temperature of saturated steam of atmospheric pressure, the volume of 1 kg. of steam will be increased to—

$$\frac{56 \times 373^\circ}{45 \times 273^\circ} = \frac{2984}{1755} \text{ cbm.} = 1.7002849 \text{ cbm.,}$$

and the weight of 1 cbm. of such steam will consequently be—

Table of Saturated Steam.

Pressure. Atmospheres.	Temperature. °N.	Weight of 1 cbm. in kg.	Volume of 1 kg. in cbm.	Heat required to evaporate 1 kg. liquid water of 0° N. Cal.	V × P.	Heat required to produce 1 cbm. of steam from water of 0° N. Calor.
0.0042	±0.000	0.003375	296.296	606.700	1.24444	2.04658
0.010	+10.000	0.007750	129.003	610.700	1.29003	4.80377
0.050	+33.960	0.035734	27.985	616.888	1.39925	22.04264
0.100	+46.000	0.06877	14.541	620.500	1.4541	42.67230
0.200	+59.997	0.13176	7.590	624.699	1.5180	82.30747
0.300	+68.328	0.19281	5.186	627.189	1.5558	120.93928
0.400	+76.327	0.25120	3.981	629.598	1.5924	158.15118
0.500	+81.940	0.30903	3.236	631.282	1.6180	185.08179
0.600	+86.592	0.36604	2.732	632.678	1.6392	231.58120
0.700	+90.591	0.42235	2.368	633.877	1.6567	267.68231
0.800	+94.091	0.47808	2.092	634.927	1.6736	303.51042
0.900	+97.201	0.53333	1.875	635.860	1.6875	339.12458
1.000	+100.000	0.588137	1.7002849	636.700	1.7002849	374.46665
2.000	+120.996	1.11359	0.88	642.999	1.7960	716.03180
3.000	+134.993	1.61308	0.620	647.198	1.8597	1043.84457
4.000	+145.491	2.09682	0.477	650.347	1.9080	1363.45964
5.000	+153.889	2.56946	0.389	652.867	1.9460	1678.30680
6.000	+160.888	3.03362	0.330	654.966	1.9776	1987.10798
7.000	+166.886	3.49096	0.286	656.766	2.0048	2293.08974
8.000	+172.135	3.94262	0.254	658.340	2.0312	2595.90064
9.000	+176.801	4.38944	0.228	659.740	2.0502	2896.09214
10.000	+181.000	4.83204	0.207	661.000	2.0696	3193.4334
15.000	+199.033	6.97096	0.143	666.410	2.1510	4646.8807
20.000	+212.500	9.03708	0.111	670.450	2.2120	6059.1322

$$= \frac{1755}{2984} \text{ kg.} = 0.5881367 \text{ kg.}$$

From these data, other properties of steam may be found by the following simple equations, where in all cases—

V denotes the volume of 1 kg. steam of any pressure in cbm.

W denotes the weight of 1 cbm. steam in kilograms.

P denotes the pressure of steam in atmospheres absolute.

T denotes the absolute temperature of steam in °N.

1. $V \times W = 1$	5. $\frac{1755 P}{8} = T \text{ (°N.)}$
2. $\frac{8 T}{1755 P} = V \text{ (cbm.)}$	6. $\frac{8 T}{1755} = P \times V \text{ (coeff.)}$
3. $\frac{1755 P}{8 T} = W \text{ (kg.)}$	7. $\frac{1}{W} = V \text{ (cbm.)}$
4. $\frac{8 W}{1755} = P \text{ (cbm.)}$	8. $\frac{1}{V} = W \text{ (kg.)}$

The accompanying Table gives, as a sample, a few of the results obtained by these formulæ, which also, in diminished scale, are shown in the diagram, and which agree very closely with M. Regnault's experiments.

(To be continued.)

3, Valdemarsgade, Copenhagen, V.
July 22, 1895.

ON THE DIRECT SPECTRUM ANALYSIS OF MINERALS AND OF SOME FUSED SALTS.

By A. DE GRAMONT.

I SOLICIT the Academy for permission to summarise the general results not only of the papers which I have already had the honour of presenting, but also of researches which are now in the course of execution.

A great number of minerals are sufficiently conductive or capable of volatilisation to give passage to the electric spark between two of their fragments connected respectively to the poles of an induction-coil with a condenser intercalated. Under these conditions the spark produced behaves in the spectroscopie like that of a metallic alloy, but giving along with the rays of the metals contained in the mineral those of the non-metals with which they are combined.

On suppressing the condenser the spectra of the non-metals disappear, and those of the metals are reduced to their most brilliant rays, showing out in general upon the luminous ground produced by the incandescence of the fragments.

A certain number of melted salts, the study of which I have undertaken, especially the haloid salts, have given the same results, which may be generalised thus:—

The condensed spark, playing on the surface of a compound, dissociates it, giving a line-spectrum generally very bright, where each substance—metallic or non-metallic—is represented by the characteristic rays of its individual spectrum. We have thus a composite spectrum, which may be considered as formed by the simple superposition of the spectra of its individual components.

The rays of the air in the condensed spark are much enfeebled in presence of the volatilised elements, especially when the explosive distance is very short; they are then reduced, practically, to the lines first signalised by Masson. These atmospheric rays have even the advantage of serving as marks for the position of the micro-metric scale.

Without a condenser and with the coil alone we have,

on the contrary, in the case of salts, complex spectra characteristic of the chemical species, and due probably to the non-dissociated molecule. They vary therefore from one compound to another. This fact has been already brought to light for salts, melted or dissolved, in numerous researches, especially those of A. Mitscherlich, Diacon, and Lecoq de Boisbaudran.

As a general method of investigation, and especially in the detection of the non-metals or in the examination of minerals, it is, in my opinion, really advantageous to make use of the condensed spark, the elements being always represented in it by the same rays, the principal of which are easily recognised at first sight.

In the case of salts the non-condensed spark gives, on the other hand, precise and very sensitive indications for detecting the presence of certain compounds by means of the band spectra.

It is, moreover, easy to suppress the condensation in the experimental arrangement employed.

For these researches we may make use of all coils; it is merely necessary to take condensers with surfaces much more considerable in proportion to the size of the coil than is generally done. For apparatus giving sparks of 3 to 5 c.m. in length, I use two, three, or four Leyden jars, each surface of which presents about 12 square decimetres.

It is curious to observe the effect of condensation upon the spark striking between electrodes coated with free non-metals: if the spark is condensed, it gives fine line-spectra of these substances *without* igniting them; if not condensed, it kindles them immediately, giving a continuous spectrum scarcely visible. This experiment is particularly striking with sulphur, arsenic, and selenium.—*Comptes Rendus*, cxxi., p. 121.

ON A PHYSICAL THEORY OF THE PERCEPTION OF COLOURS.

By GEORGES DARZENS.

IN order to explain the perception of colours, Young, and subsequently Helmholtz, admitted that each fibre of the optic nerve which enters into a cone of the retina is composed of three fibrils, one of which is strongly excitable by the red and little by the green and the violet; the second strongly excitable by the green and little by the red and the violet; and lastly, the third is strongly excited by the violet and little by the red and the green.

This hypothesis accounts for the existence of three elementary colours; it equally explains a certain number of other facts, such as some peculiarities observed in dyschromatopsies, the phenomena of saturated colours, &c. But it is unable to explain many other facts not less important. Why should light having a wave-length of $\mu 0.620$ strongly excite one of these fibres and have scarcely any effect upon the two others?

Here is a new theory of luminous perceptions which seems to me to agree better with the progress of physical optics and of physiology.

A luminous ray, after having traversed the different strata of the retina, impinges normally upon the pigmentary layer of this membrane; there it is reflected, and interferes with the incident ray. Hence we must have there in front of the pigmentary layer, and consequently in the actual thickness of the retina, a system of stationary waves distant by $\frac{\lambda}{2}$, as in the experiments of O.

Wiener, or in those of Lippmann on the photography of colours. It is further probable that these stationary waves can exist only in a feeble thickness, on account of the absorption by the medium which constitutes the retina.

Let us remark, in passing, that this specular function of the pigmentary layer exists in an unquestionable manner in the ox, where it constitutes the "carpet." These stationary waves excite the nervous terminations of the optic nerve. These terminations are of two orders, the rods and the cones.

The rods being constituted by cylindric fibrils, respectively parallel, we can conceive that the stationary waves will excite them all, whatever may be their position—that is, whatever may be the λ of the incident light. Hence we conclude that the rods give to the brain the general notion of light, without enabling us to judge of its colour. We know that the brain always conveys its excitements to the circumference, whatever may be the place where the nerve has been excited.

The cones, on the contrary, being formed of fibres, parallel, but unequal in length, will be excited differently according to the λ ; they will enable the brain to take account of the colour.

These two conclusions are fully verified by experiment. It is known that we do not perceive all the colours well except by the central part of the retina (the yellow spot). Now it is there where the cones are found, the rods being turned towards the equator of the retina, which gives merely the sensation of light without the notion of colour.

On the other hand, nocturnal animals which do not distinguish colours have no cones, whilst in birds which feed on coloured insects the retina is rich in cones.

Finally, if this theory is correct, whenever the pigmentary layer disappears, whether by old age or disease, there must result a parallel enfeebling of sight (a chromatopsy). This is apparently confirmed by experience.

This new theory can be brought to harmonise with the hypothesis of Young and Helmholtz. We need merely admit that the fibrils of the cones are divided into three groups proceeding to three different centres of perception. Still more, it explains why the wave-length which strongly excites one of these groups of fibrils must excite the other two groups feebly. It explains that curious arrangement of the retina when the excitable elements (cones and rods) are found placed in the deepest stratum, turned, so to speak, away from the side of the pigmentary layer which has hitherto appeared inexplicable.

It is remarkable to note that the procedure employed by the eye, in taking account of the wave-length of a ray of light, is quite comparable with the procedures hitherto employed by physicists.

To me this theory appears satisfactory to reason, since it reduces the perception of colours to the appreciation of a wave-length which is a magnitude of an order comparable to the dimensions of the anatomical elements of the retina. It further seems to me to throw a clear light on the explanation of a number of the peculiarities of the eye.

To cite merely a single instance, in the study of the achromatism of the eye we must no longer consider the retina as a simple screen like those of our laboratories, but a screen which perceives the different colours in different zones.—*Comptes Rendus*, cxxi., p. 133.

ILLUMINATION BY LUMINESCENCE.

By A. WITZ.

LUMINOUS foci are constituted by an incandescent solid or liquid, the temperature of which, according to Draper, must exceed 1100° , in order that the light may be white and the spectrum complete. The visible has for its boundaries the wave-lengths 0.38 and 0.76μ , but the infra-red extends, so to speak, indefinitely towards the less refrangible radiations, giving out a heat sensible to Langley's bolometer as far as to waves of the length of

30μ , and consequently including more than five octaves of luminous radiations. If we trace the curve of energy of the spectra, plotting out the wave-lengths as abscissæ, and the intensities of the radiations as ordinates, we find that it presents only a single maximum, situate generally at the beginning of the infra-red, but which is displaced progressively and advances towards the most refrangible region as the temperature of the focus increases. This curve is not symmetrical with reference to the maximum ordinate, and the greater part of its area lies on the side of the dark heat-spectrum. A large proportion of the energy belongs, therefore, to these invisible and hot radiations. This is the reason why foci of light are all at the same time foci of heat, the photogenic yield of which is extremely slight. I have calculated this yield in a paper inserted in the *Comptes Rendus* (cxii., June 29, 1891).

To improve this yield would be an important scientific discovery, and a great number of investigators have made it the object of their researches.

It has appeared to some that the solution of the problem might be furnished by luminescent foci, in which the temperature of the rarefied gas is, according to Herr Warburg, included between 21° and 132° . These foci, it must be admitted, radiate but little light, but their thermic emission is still more feeble.

The luminescence of the tubes is effected either by the high tension currents given by Volta-Faradaic induction apparatus, or by the currents supplied by a Holtz machine. In the former case we may determine the watts consumed in the tube; in the second case we measure the kilogrammeters expended to set the generating machine in action, both when at liberty and when burdened.

I have experimented with several tubes, and especially with a lamp intended for miners and a tube for physicians (for illuminating deep cavities of the body).

The lamp for miners is illuminated without difficulty by the induction current of a small Ruhmkorff coil, yielding a spark of 20 m.m.; it yields enough light to read a table of logarithms at the distance of 40 c.m. from the source of light. Mr. Langley has been content with this very rudimentary photographic measurement. The pale greyish blue tint of the light does not lend itself to the methods of comparison used in photometry. I have found between the terminal electrodes a difference of potential of 4190 volts, the current having then an intensity of 0.27 milliampère, which makes 1.13 watt. The energy consumed is large in comparison with the light produced; we might hope for a better yield.

The results obtained with a Holtz machine are more interesting. I have used Hirn's transmission dynamometer to determine the work necessary to make the glass plate of the machine rotate 726 times per minute, under the following conditions:—

Movement.		Sparks of	
Free. circuit on	Closed 145 m.m.	8 per	Miner's Medical
machine. second.		lamp. tube.	

Work per second
in kilogrammeters 1.043 1.785 2.174 1.711 1.763

Hence the illumination of the miner's lamp requires $1.711 - 1.043 = 0.668$ kilogrammeters, or 6.6 watts. The yield is still less than that above. The incandescence of a lamp with a carbon filament in a vacuum only requires 3 watts per candle. Our miner's lamp absorbs more energy and gives much less light—a ruinous method of lighting. Still the quantity of heat radiated is slight.

Having plunged the medical tube into a calorimeter, we have observed a liberation of 0.00033 cal. per second, which corresponds to $0.00033 \times 425 = 0.140$ kilogrammeter. Now, the illumination of this tube requires 0.720 kilogrammetre, whence the heat produced corresponds only to the fifth part of the energy expended. From this point of view no other source of light gives so favourable a result.

The figures which we produce are evidently only a first approximation, since they vary with the nature and the form of the tubes employed, and have no absolute character. But we may learn from our experiments that, in lighting by luminescence, the proportion of thermic energy with reference to the entire energy is smaller than in any other source of light. By reducing to a minimum the losses of electricity, by concentrating the light in a limited space, by utilising the fluorescence of certain substances, by inventing certain special arrangements, we may hope to obtain foci the photogenic yield of which will be greater than that of our best sources of light. At present luminescence at low temperatures gives but very mediocre results, but at least enables us to reduce the invisible and useless portion of emission spectra.—*Comptes Rendus*, cxxi., p. 306.

ANG-KHAK, A CHINESE FUNGOID PIGMENT, USED FOR COLOURING ARTICLES OF FOOD.

By H. C. POINSEN.

THIS colouring-matter is imported into Java from China, for giving a fine purple colour to foods and beverages. It is the product of a special fungus which is propagated in the province of Quant-tung for preparing the colouring-matter. Rice, thoroughly boiled, is spread out upon plates to cool, and when quite cold is sprinkled over with ang-khak of a former preparation. The plates, with their contents, are then kept for six days in a dark, cold place. It then has a red colour, which afterwards becomes darker.

In what manner the Chinese obtained the first ang-khak fungi is unknown. The colouring-matter dissolves readily in alcohol with a splendid garnet-red colour. The fungus belongs to the group of the *Telebolæ*. It vegetates upon any kind of carbohydrate in the presence of oxygen. The chief difficulty in its preparation is to keep away other fungi and bacteria, especially a species not yet examined. This is effected by means of a trace of arsenic, which prevents the growth of other bacteria without interfering with the development of the ang-khak.

The colouring-matter can be extracted with chloroform. In a state of purity it dissolves in methyl- and ethyl-ether, glacial acetic acid, acetone, and ethyl acetate, but very sparingly in water and dilute acids, and not at all in benzene, petroleum ether, oil of turpentine, carbon-disulphide, and glycerin. It melts at 50°, and at a strong heat it is decomposed without subliming. The alcoholic solution displays a narrow absorption band at D, and a broad band in the blue between D and G. The colouring-matter behaves like most of the aniline colours, but it is distinguished by its precipitability with mercuric oxide.

(The manufacture of ang-khak is probably the first instance of the technical use of microbia).—*Chemiker Zeitung*.

PREPARATION AND PROPERTIES OF HYDRAZIN HYDRATE.

By C. A. LOBBY DE BRUYN.

THE isolation of hydrazin hydrate without the use of silver vessels is effected as follows:—

The commercial hydrate is first converted into the more readily soluble hydrobromic compound by means of barium bromide; the precipitate is filtered off, and the filtrate is concentrated by evaporation and gradually mixed with the calculated quantity of concentrated potassium lye. After the liquid has been diluted with an

equal volume of alcohol it is allowed to cool; the potassium bromide is filtered off with the aid of the pump, rinsing out with a little alcohol. The filtrate is distilled at ordinary pressure until the ebullition point reaches 108°. We have thus the chief part of the base in the residue, in which potassium bromide further separates out on cooling.

After filtration it is distilled at first at the ordinary pressure, and then at a pressure of 121 to 122 m.m. Of the six fractions collected the three last contain from 77 to 97.5 per cent of hydrazin hydrate. To this mixture there is added, after heating to 50°, rather more than the calculated quantity of barium oxide to combine with the water present, when a strong heat is developed. After cooling there is added, to each 150 grms. of the hydrazin sulphate employed, 20 to 25 c.c. of absolute alcohol; it is filtered and washed with a little absolute alcohol. The solution is then fractionated at a reduced pressure, when about 22 per cent of the theoretical yield contains 99.7 per cent of hydrazin hydrate, free from silicon.

The boiling-point of hydrazin hydrate, at a pressure of 26 m.m., is constant at 47°. There is no perceptible decomposition. In air free from carbonic acid, hydrazin hydrate is slowly oxidised with an escape of gas. The substance dissolves various salts, such as potassium bromide, iodide, and cyanide; ammonia, sodium chloride, and salts of lead with difficulty, whilst potassium and zinc sulphates are scarcely taken up at all. Sulphur is gradually dissolved, even by dilute solutions; salts of lead gives a black deposit with the solution.

On boiling hydrazin hydrate at 22.8 per cent with sulphur the liquid takes a reddish-brown colour, whilst sulphuretted hydrogen escapes. From this solution sulphur is thrown down, not by water, but by an excess of hydrochloric acid. Phosphorus acts slowly upon hydrazin hydrate, and an odour of hydrogen phosphide is given off. Sodium decomposes hydrazin hydrate with the formation of hydrogen and ammonia, and there separates out a crystalline substance soluble in water and alcohol. The solution of the substance gives the hydrazin reactions. —*Rec. Trav. Chim. des Pays Bas* and *Chem. Zeitung*.

REPORT OF COMMITTEE ON ATOMIC WEIGHTS, PUBLISHED DURING 1894.*

By F. W. CLARKE.

(Continued from p. 95).

BARIUM.

RICHARDS has corroborated his earlier determinations of the atomic weight of barium, which were made with the bromide, by means of additional series of experiments upon the chloride (*Proc. Amer. Acad.*, xxix., 55). The work was carried out in the most elaborate and thorough manner, and for details the original paper must be consulted. First, barium chloride was titrated with standard solutions of silver, and the several series represent different methods of ascertaining accurately the end point. The data are as follows, with the ratio $\text{Ag}_2 : \text{BaCl}_2 :: 100 : x$ in the third column.

First Series.		
Wt. Ag.	Wt. BaCl ₂ .	Ratio.
6.1872	5.9717	96.517
5.6580	5.4597	96.495
3.5988	3.4728	96.499
9.4010	9.0726	96.57
0.7199	0.6950	96.541
Mean ..		96.512

* From the *Journal of the American Chemical Society*, vol. xvii., No. 3. Read at the Boston Meeting, Dec. 28, 1894.

Second Series.

6'59993	6'36974	96'512
5'55229	5'36010	96'539
4'06380	3'92244	96'522

Mean .. 96'524

Third Series.

4'4355	4'2815	96'528
2'7440	2'6488	96'531
6'1865	5'9712	96'520
3'4023	3'2841	96'526

Mean .. 96'526

Fourth Series.

6'7342	6'50022	96'525
10'6023	10'23365	96'523

Mean .. 96'524

All the weights represent vacuum standards. From the four series the atomic weight of barium is deduced as follows; when O = 16.

First series	Ba = 137'419
Second	" 137'445
Third	" 137'449
Fourth	" 137'445

In three more series of experiments Richards determined the ratio between 2AgCl and BaCl_2 . The data are subjoined, with the ratio $2\text{AgCl} : \text{BaCl}_2 :: 100 : x$ appended.

First Series.

Wt. AgCl.	Wt. BaCl ₂ .	Ratio.
8'7673	6'3697	72'653
5'1979	3'7765	72'654
4'9342	3'5846	72'648
2'0765	1'5085	72'646
4'4271	3'2163	72'650

Mean .. 72'649

Second Series.

2'09750	1'52384	72'650
7'37610	5'36010	72'669
5'39906	3'92244	72'650

Mean .. 72'6563

Third Series.

8'2189	5'97123	72'6524
4'5199	3'28410	72'6587

Mean .. 72'6555

Hence we have for Ba—

First series	Ba = 137'428
Second	" 137'446
Third	" 137'444

The mean of all is 137'440, as against 137'434 found in the work on the bromide. By combining the two chloride ratios, $\text{Ag}_2 : \text{BaCl}_2$ and $2\text{AgCl} : \text{BaCl}_2$, the ratio $\text{Ag} : \text{Cl}$ can be computed. This gives $\text{Ag} = 107'930$, a value identical with that of Stas.

(To be continued).

Detection of Ergot in Bran.—The method of E. Hofmann, according to Ulbricht, is useless if bran contains the seeds of *Polygonum convolvulus*. The author finds that 0.2 per cent of ergot, and even smaller quantities, can be detected microscopically if the bran is previously digested for two hours on the water-bath with sulphuric acid at 1.25 per cent, then with soda-lye of the same strength, and, lastly, treated in the cold with absolute alcohol and ether.—*Zeit. Anal. Chem.*, xxxiii., Part 6.

THIRTEENTH ANNUAL REPORT
OF THE COMMITTEE ON INDEXING
CHEMICAL LITERATURE.*

THE Committee on Indexing Chemical Literature presents to the Chemical Section its Thirteenth Annual Report.

During the twelve months which have elapsed since the last report the following bibliographies have been printed:—

1. "Indexes to the Literature of Cerium and Lanthanum." By W. H. Magee. *Smithsonian Miscellaneous Collections*, No. 971. Washington, 1895. 43 pp. 8vo.

2. "Index to the Literature of Didymium, 1842—1893." By A. C. Langmuir. *Smithsonian Miscellaneous Collections*, No. 972. Washington, 1895. 20 pp. 8vo.

These bibliographies of three associated metals fill an important gap in chemical literature. That by Dr. Langmuir is reprinted from the *School of Mines Quarterly* (vol. xv.), at the request of your Committee. Both indexes are arranged chronologically and provided with author-indexes.

3. "Bibliography of Aceto-Acetic Ester." By Paul H. Seymour. *Smithsonian Miscellaneous Collections*, No. 970. Washington, 1894. 148 pp. 8vo.

This bibliography was compiled by the author under the direction of Prof. Albert B. Prescott, and by him submitted to the Committee who recommended its publication Aug. 22, 1892. It consists of a series of carefully prepared, critical abstracts of original papers arranged chronologically with author- and subject-indexes.

After issuing the twelfth Annual Report the attention of the Committee was directed to two contributions to the bibliography of chemical and pharmaceutical periodicals by Dr. Friedrich Hoffmann, editor of *Pharmaceutische Rundschau*, viz.:—

4. "Die Deutsch-sprachlichen pharmaceutischen Zeitschriften." *Pharm. Rundschau*, New York, vol. xii., pp. 7—10 (Jan., 1894), and p. 28 (Feb., 1894).

5. "Englisch-sprachliche pharmaceutische, chemische und botanische Zeitschriften Nord-Amerika's." *Pharm. Rundschau*, New York, vol. xii., pp. 131—136 (June, '94).

Several chemists have made reports of progress:—

Prof. Henry Trimble, of Philadelphia, states he continues to collect references to the literature of the Tannins with the expectation of further publication at no very distant date.

Prof. Arthur M. Comey reports that his "Dictionary of Solubilities," vol. i., is nearly all in type, and should appear early in the autumn.

Dr. Alfred Tuckerman expects to complete the MS. of his "Index to the Mineral Waters of all Nations" in a few months.

Prof. F. W. Clarke is making progress with a new edition of the "Re-calculation of the Atomic Weights."

Dr. H. Carrington Bolton reports having done much work on the Supplement to his "Bibliography of Chemistry," the MS. now comprising about 6500 titles.

Mr. C. LeRoy Parker, of the Columbian University, Washington, has undertaken an "Index to the Literature of Attempts to Decompose Nitrogen."

Mr. George Estes Barton, of the same Institution, is at work on a "Bibliography of Glycerol"; and Mr. George Baden Pfeiffer, also of the Columbian University, is engaged on a "Bibliography of Picric Acid and the Nitrophenols."

At the request of the Smithsonian Institution Dr. H. Carrington Bolton has undertaken to edit a new edition of his "Catalogue of Scientific and Technical Periodicals, 1665—1882," published in 1885 in the *Smithsonian Miscellaneous Collections*. The new edition will bring

* Advance sheets from *Proceedings Amer. Assoc. Adv. Sciences*, vol. xlv., communicated by Professor H. Carrington Bolton.

down to date the old periodicals and include new ones established since 1882. The work is well under way.

Mr. W. D. Bigelow, of the Chemical Division of the U.S. Department of Agriculture, has completed the MS. of an "Index to Methods for the Detection and Estimation of Fusel Oil in Distilled Liquors." The channel of publication has not been determined.

In a communication to the chairman, Prof. W. Percy Wilkinson, of Melbourne, states he is engaged on an "Enological Biography," to include works relating to the vine, viticulture, wine-making, vine-diseases, and wine-analysis, published in Germany, France, England, America, Italy, Portugal, and Spain. He expects the bibliography to number 2000 titles, and will give full details as to date, size, editions, &c. It is to be published by the Royal Society of Victoria.

Monsieur G. Fr. Jacques Boyer, Editor of the *Revue Scientifique*, Paris, announces the preparation of a "Bibliography of Physical and Chemical Science"; information as to its scope and period is lacking.

Those interested in the chemical applications of electricity should note the following:—

"Elektrotechnische Bibliographie; monatliche Rundschau über ... der Elektrotechnik." Von Georg Maas. Leipzig, 1893.

Also: "Lehrer's Elektrotechnischer Katalog . . . von 1884 bis 1893." Leipzig, 1893. 8vo.

The following special bibliography has recently appeared in France:—"Bibliographie de la technologie chimique des fibres textiles. Propriétés, blanchiment, teinture, matières colorantes, impression, apprêts." Par J. Garçon. Paris, 1893. 8vo. This work has been honoured with a prize by the Société Industrielle de Mulhouse.

Although not pertaining to chemistry, we may briefly note the appearance of another special bibliography:—"Bibliographie der psycho-physiologischen Litteratur des Jahres 1893." Hamburg, 1894. 8vo. Published in the *Zeitschrift für die Psychologie und Physiologie der Sinnesorgane*.

Attempts to establish a comprehensive Index to Chemical Literature in the form of a periodical are not altogether successful, lacking the important element of permanence. The "Index" announced by Dr. Bechhold, of Frankfurt-on-Main, noticed in our Twelfth Report, has not made its appearance; the *Biblioteca Polytechnica*, by Szcsepanski, ceased at the close of one year; the *Universal Index*, by Wien and Brockhaus, reached only nineteen numbers. Dr. J. Ephraim advertises the following, "Index der gesamten chemischen Litteratur (Wissenschaft und Technologie), Berlin," but no number has yet appeared.

Committee:—

H. CARRINGTON BOLTON, Chairman,
F. W. CLARKE,
ALBERT R. LEEDS,
ALEXIS A. JULIAN,
JOHN W. LANGLEY,
ALBERT B. PRESCOTT,
ALFRED TUCKERMAN.

August, 1895.

On Hexamethylenetetramine.—R. Cambier and A. Brochet.—Among the interesting properties of hexamethylenamine, the authors mention the formation with bromine and iodine of the addition-compounds $C_6H_{12}N_4X_2$ and $C_6H_{12}N_4X_4$. The compounds with X_4 , being very unstable, lose in part their haloid element on mere exposure to air. Nitrous acid reacts upon hexamethylenamine and forms in the first place dinitrosopentamethylenetetramine, which is decomposed by acids and yields nitrogen, ammonia, and formic aldehyd. Hexamethylenamine, if treated by acids, is easily split up by hydration into its components.—*Bull. Soc. Chim. de Paris*, xiii.-xiv., No. 4.

NOTICES OF BOOKS.

An Introduction to the Study of Disinfection and Disinfectants. Together with an Account of the Chemical Substances used as Antiseptics and Preservatives. By SAMUEL RIDEAL, D.Sc., F.I.C., F.C.S., &c. 8vo., pp. 316. London: Charles Griffin and Co., Lim. 1895.

The author of the work before us sets out with distinguishing between disinfectants, antiseptics, and deodorants, classes of substances often confounded. Charcoal he classes not among disinfectants, but with the deodorants. The problem of disinfection he shows is a struggle for existence between men and the pathogenic microbia, which, despite their minuteness, rank among our most formidable enemies. The methods of solving this problem are classed under the heads of exclusion, removal, and destruction.

Under the head of Mechanical Disinfection the author enumerates a number of substances used as filter-beds, or in the treatment of faecal matters and of impure waters. It is mentioned that light has a destructive action on bacteria, and even to some extent on their spores. Hence, as Dr. Percy Frankland rightly insists, every opportunity should be used for insolation in the construction of water-works, and, we must add, of works for the treatment of sewage.

The value of charcoal, animal and vegetable, is duly recognised. The former is credited with removing the ptomaines and a number of other hurtful organic compounds. The action of certain residual carbons is very similar. The remark that "a large number of processes have endeavoured to recover the phosphate (of sewage) by using the sludge as a fertiliser, but they have all met with little commercial success," we must pronounce utterly mistaken. Soot is rightly said to have no great power, and coal-dust is with equal correctness proclaimed to be almost inert. The value of peat is fully recognised, but in the treatment of sewage care, we must urge, should be taken to avoid pyritic samples, such as those of some districts of Berks.

Sterilised sand, according to Fränkel and Piefke, does not retain microbia.

The Chamberland and Berkefeld filters—the latter made of infusorial earth, compressed and baked—are recommended for household use, but filters of stone and of asbestos are condemned, views which our experience enables us fully to endorse.

The process of Scott Moncrieff has been tried and abandoned at Aylesbury.

The process of disinfection by means of hot air and steam is described at some length, with the addition of illustrations showing the plant employed. Incinerators, or destructors for dust, &c., are also noticed.

The fourth chapter discusses chemical disinfectants. The opinions recorded concerning different agents and processes are far from agreeing. The Hermite process is judged unfavourably by Sir H. Roscoe and Lunt (p. 69), and by Dr. Kelly, the medical officer of health at Worthing, who incorporates the chemical and bacteriological analyses of Drs. Dupré and Klein. Chamberland and Fernbach allege that eau de Javelle (1:120) and commercial hydrogen peroxide are more effective than mercuric chloride against pathogenic microbia.

The important caution is given that sodium chloride is not a disinfectant, and that brine sometimes acquires a high degree of toxicity. This is the more important as we have observed that stale brine is often kept and used for salting successive quantities of bacon, hams, fish, &c. On the comparative value of the halogens opinions differ.

On chloroform, which has even been proposed for the treatment of sewage, Dr. Rideal remarks that its cost and its poisonous action on animals render it of very limited application.

The author recognises that "polluted water flowing over weirs and waterfalls is oxidised and becomes clear and brilliant," and again that "the self-purification of rivers in this way is now accepted by most chemists, the natural aëration being aided by Infusoria and vegetation in removing most of the dead organic matter, and in reducing the number of micro-organisms present." These conclusions will meet with the approval of observant and unbiased students of the sewage question.

Sulphate of lime is rightly condemned as an ingredient in mixtures for the precipitation of sewage. It has the serious disadvantage—not mentioned here—of injuriously affecting the health of the men employed in sewage-works. To find zinc salts still used in the disposal of sewage is deplorable.

The process Patent No. 11641 (1884), is travestied so as to give a very misleading impression of its nature. The summary of sewage precipitation processes given by Parkes and Corfield (p. 129) must be taken with a very large grain of salt.

We regret that we cannot further examine this able and interesting work. Its weakest side is its criticism of processes for the treatment of sewage.

Alkali, &c., Works Regulation Act, 1881. Thirty-first Annual Report on Alkali, &c., Works by the Chief Inspector. Proceedings during the Year 1894, presented to the Local Government Board and to the Secretary for Scotland. London: Her Majesty's Stationery Office.

THIS Report is drawn up with great care and accuracy, and contains both alarming and reassuring features. The number of works in England, Ireland, and Wales, as now registered, is 1056, of which only 102 are alkali-works proper, whilst 954 fall within the schedules of other establishments recently included under the provisions of the Act. Since 1893 there has been an increase of one alkali-works and nine other works. In Scotland there are 126 registered works, making a grand total of 1182.

The number of processes of manufacture which fall within the provisions of the Act is now 1520. The separate processes are:—Alkali, copper (wet process), sulphuric acid, chemical manures, gas liquor, nitric acid, sulphate and muriate of ammonia, chlorine and bleaching-powder, sulphur recovery, salt, cement, alkali waste, barium and strontium, antimony sulphide, bisulphide of carbon, Venetian red, lead deposit, arsenic, nitrate and chloride of iron, muriatic acid, fibre separation, tar and zinc smelting.

One most offensive process, of no national importance, has escaped attention,—to wit, ballast-burning, which, in most of the outskirts of London, fills the air with nauseating fumes, and which ought to be totally suppressed in all urban districts.

The visits of inspection to scheduled works are made about once monthly, unless there is apparent need for a closer investigation. In alkali works and sulphuric acid works definite limits are fixed as to the amount of acid fumes which may lawfully escape. In other cases the Act merely requires that the best practicable means for preventing the escape of noxious gases and vapours should be employed.

The Report shows that the amount of hydrochloric acid in the chimney gases is less than one-half, the limit allowed by law; whilst in case of sulphuric acid the escape is only about one-third of the legal margin. These facts are doubly satisfactory, as showing, on the one hand, that the standards fixed are reasonable, and, on the other hand, the watchful attention of the inspectors and the loyal compliance of the manufacturers.

Two successful prosecutions have been conducted and fines inflicted for evasions of the enactment that the inspector is to have full access to all apparatus used in carrying out the operations.

It is satisfactory to learn that the Leblanc works hold

their own in virtue of the chloride of lime which they only are as yet able to produce.

The effects of the coal-strike of 1893 are still felt. The salt decomposed in the Leblanc process was in the year 1892 519,593 tons, but has now fallen to 434,298 tons. On the other hand, the salt consumed in the ammonia process has risen in the same time from 304,897 tons to 361,603 tons. Thus the gain of the ammonia process is far from explaining or compensating the decline of the Leblanc process. The electric alkali process, if the required energy has to be obtained from coal, is an amusing scientific version of the "House that Jack built." But the writer shows that where water power is cheap and abundant,—e.g., Italy, Switzerland, South-eastern France, Norway, as well as the Dominion and the United States,—both Leblanc and Solvay may find themselves in jeopardy.

The ammonia lost by our wasteful system of coal-burning was estimated by Dr. Angus Smith at £50,000,000. A yearly economy in this direction, to the extent of £2,000,000, has already been secured.

In the treatment of tank-waste the Chance-Claus process works successfully. At Widnes, St. Helens, &c., raw waste is no longer deposited on the land—a subject for public congratulation. But old beds of tank-waste, where they have been used for filling up hollows and making embankments, still remain, and if they come in contact with acid leakage serious accidents may occur. A fatal case took place lately at Irvine, and is here recorded.

The manufacture of nitric acid is experiencing extension. Mr. Manning Prentice, of Stowmarket, has made the process continuous, thus effecting at once economy and a suppression of possible nuisance.

Coal-smoke is not a substance of which the inspectors under the Alkali Act have to take official cognisance. But they are obliged to examine it, as its effects are too often ascribed by the public to the emanations from chemical works. About a million tons of coal are burnt yearly at Widnes. This coal contains about 14 per cent of sulphur, and thus generates 30,000 tons of sulphurous acid, which is diffused over the country. The effects of a sooty atmosphere and of sulphurous acid are rightly considered by Mr. Fletcher, the chief inspector, as taking no small share in the injury to vegetation. He thinks that the "open fire is incorrigible," and he fears that the love of an Englishman for the cheerful blazing fire will stand in the way of any reform. He mentions, however, the case of "one house, inhabited by a large family, where recently, during a week of frosty weather, twenty-one open fires and five oil or gas stoves were kept burning." He thinks that one of the twenty-one fires, if burnt in a properly constructed stove, would have heated the whole house better than the twenty-one in open grates.

In a passage quoted from *Die Chemische Industrie*, on the health of the workmen employed by the Griessheim Chemical Co., it is declared, on the authority of Dr. C. Wolff, for ten years medical officer to the works, that—"As in former years, artisans such as carpenters, coopers, smiths, &c., show a higher percentage of sickness than the process men," i.e., those employed in the manufacture of sulphuric acid, hydrochloric acid, nitric acid, soda-ash, caustic soda, nitrobenzene, picric acid, chromates, &c.

We have every reason to conclude that the present Chief Inspector, Mr. A. E. Fletcher, and his colleagues are proceeding on the lines laid down by his distinguished predecessor, Dr. R. Angus Smith.

Report of the Dairy Commissioner of the State of New Jersey. For the Year 1894. New Jersey: Trenton.

THIS Report will be of the greatest value to sanitary chemists. We find that in the United States the liability of milk to pollution and its danger to public health are

fully recognised by the Courts, by men of Science, and even by the general public. We fear that in this last respect we, in this country, do not hold the first rank. Strict legislation and analytical skill, chemical and micro-biological, fall short of their aim unless supported by enlightened public opinion.

But in America very much remains to be done. We learn that "the standard of 12 per cent solids is so low that most whole milk can be watered—and much is—with great precision, so as just to escape the penalties of the law." In Hudson and Essex counties nearly 2500 stables were found by the inspectors, in most of which the cattle were kept in a crowded and unhealthy condition, and in which the principal food was wet and soured brewers' grains. The Commissioner proposes raising the standard to 12.5 per cent total solids, with a minimum of 3.5 per cent of fat.

The importance of cleanliness in cow-houses and dairies is now beginning to be appreciated. In some establishments the cattle are groomed previous to milking; their udders are washed; the milkman is required to exchange his ordinary working clothes for a clean-washed smock, and to wash his hands and remove the offensive dirt from his finger-nails (which is otherwise—*horribile dictu*—washed out by the warm milk and carried into the pail). But even this improvement falls short of what is needed. It is truly remarked that when straw becomes damp and filth-stained, and then raised to the temperature of blood-heat by the cattle lying upon it, such straw becomes a most prolific breeding-ground for bacteria. "Every movement of the cow and the milkman raises up a cloud of bacterial dust from the bedding, and until a substitute is provided this dust will continue."

It may be asked whether peat-litter might not be found in this respect preferable to straw? It is proposed to dispense with bedding altogether, and let the cows lie on a clean inclined plank floor, made waterproof and with the seams caulked, all excreta being forthwith removed.

An interesting fact here mentioned is that, with a nearly identical food, the best cow produced 2½ times more milk and 3 times more butter than the poorest cow (referring to certain experiments performed at Kildebrønne, in Denmark).

From facts ascertained we learn the importance of refrigerating milk before being conveyed to consumers.

Mention is made of pasteurised milk, of sterilisation, and of a "certified milk" the preparation of which has been described in a former report, and in which the number of bacteria per c.c. is only a few hundreds instead of from 10,000 to 60,000 bacteria. The alleged sterilisation is sometimes illusive.

None of the brands of condensed milk here described are known in Britain.

The Pharmaceutical Journal of Australasia. Vol. VIII., No. 5.

THE interesting fact in this issue is the opening of chemical works by Messrs. Elliott, at Brisbane. The immediate object of the firm is the production of sulphuric acid, the freight of which from Britain may be considered prohibitory. No information is, however, given as to the supply of pyrites, its quantity and quality.

Ultior objects of the firm are the manufacture of potassium cyanide, the nitrogenous matter being the refuse from the meat works; the production of compressed carbonic acid, and that of superphosphate. For all these products there cannot fail to be a large opening in Australia.

The Atomic Weights of Nickel and Cobalt.—Clemens Winkler.—The author finds the atomic weight of nickel, as calculated from the mean result of his experiments, 58.7433, and that of cobalt 59.3507. These atomic weights are referred to H=1 and I=126.53. *Zeit. Anorg. Chemis.*

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxi., No. 6, August 5, 1895.

Illumination by Luminescence.—A. Witz.—(See p. 104).

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xiii.-xiv., No. 4, 1895.

Nickel and Cobalt Sulphides.—A. Villiers.—Already noticed.

Qualitative Separation of Nickel and Cobalt.—A. Villiers.—Already noticed.

Protomorphic States of Zinc and Manganese Sulphides.—A. Villiers.—Already noticed.

Researches on the Basic Nitrates.—M. Athanescou.—The author finds that the process of which he has spoken in a former paper is not novel, but had been previously employed by other chemists. His objects have, however, been different. He seeks to show that the basic compounds contain hydroxyls attached to the metals which they completely saturate, and that very often in the conditions of the formation of the basic salts the plurivalence of the atoms takes always a preponderating part in the direction that, in place of obtaining compounds derived from anhydrides of the first, second, or third degree, we may obtain them corresponding to the highest degree of hydration of the non-metal. He turns his special attention to the lead nitrates.

On the 2-Ethyl-4-Methylpentanoic Octylic Acid.—Ph. A. Guye and J. Jeanprêtre.—Not adapted for useful abstraction.

Active Amylactic Acid and some of its Derivatives.—Mdle. I. Welt.—The chief result of these experiments relates to the ethers of amylactic acid. If we calculate the values of the product of asymmetry of the methylic and ethylic ethers, we find decreasing numbers; it is the same with the rotatory powers. We cannot, then, meet with in this series an ether with a maximum rotatory power, as the first term is already on the descending branch of the curve.

Contribution to the Study of the Tartaric Ethers.—Ph. A. Guye and J. Fayollot.—Already noticed.

New Process of Preparing α -Naphtholsulphonic Acid, $C_{10}H_6.OH.H.SO_3$ 1-4.—Fred. Reverdin.—None of the procedures hitherto employed are founded upon the direct sulphonation of α -naphthol. The author and his colleague, De la Harpe, have found the carbonic ether of α -naphthol an excellent primary material for the preparation of naphtholsulphonic acid 1-4. In the industrial production, carbon oxychloride is passed at the common temperature into a solution of—

α -Naphthol..	60 kilos.
Soda-lye ..	60 "
Water ..	1000 "

Sulphonated Colouring Matters derived from Triphenylmethane.—Maurice Prud'homme.—The author's experiments establish the complete parallelism between the series of rosaniline and its derivatives and the corresponding series of sulphonated rosaniline, and support the constitutional formulæ which Rosenstiehl has proposed for these two classes of substances. All the properties of magenta which I have pointed out re-occur in the bases of malachite green and of hexamethylated violet. All those of acid magenta re-occur in acid green and magenta and in Nicholson blue. The alkaline salts of sulphonated, cyanido, and triamido triphenylcarbinols are colourless.

These substances may be considered as hydrated organic bases. The salts of these bases, where the hydroxyl may be replaced by an acid radicle, are coloured. Acid magenta is, or may be, according to proportions of hydrochloric acid added to the colourless alkaline salt, a mixture of $\text{HO}-\text{C}\equiv(\text{C}_6\text{H}_5.\text{SO}_3\text{Na}.\text{NH}_2)_3$ (colourless) and of coloured $\text{Cl}-\text{C}\equiv(\text{C}_6\text{H}_5.\text{SO}_3\text{Na}.\text{NH}_2)_3$, or even of this latter body and $\text{Cl}-\text{C}\equiv(\text{C}_6\text{H}_5.\text{SO}_3\text{H}.\text{NH}_2)_3$ (coloured).

Insufficiency of Kjeldahl's Method for Determining Nitrogen in the Chloroplatinates.—M. Delépine.—Already noticed.

No. 7, 1895.

This issue contains a long notice of the life and researches of E. A. Rigout, a distinguished chemist who died in August last at the age of seventy-five. During the year 1871 he had remained alone in charge of the Ecole des Mines, and at no small risk to his life he contrived to save this establishment from destruction.

On the Cryohydrates.—A. Ponsot.—After a careful and prolonged examination the author concludes that the cryohydrates of Guthrie do not exist, but are merely mixtures of pure ice and of a solid salt, hydrated or anhydrous.

Influence of Temperature and of the Ambient Medium on the Transformation of Amorphous Zinc Sulphide.—A. Villiers.

Method of Determining the Crystallisation of Precipitates, Zinc and Manganese Sulphides, Manganese Hydroxide.—A. Villiers.—Already noticed.

Oxides and Sulphides having an Acid and a Basic Function. Zinc Sulphide.—A. Villiers.—The study of the properties of oxides and sulphides has led us to think that the acid and alkaline functions which may be fulfilled by indifferent oxides and by some sulphides do not belong, at least in a number of cases, to one and the same substance, but to two varieties, distinct in their chemical and physical properties. In the case of precipitated zinc sulphide, we may distinctly recognise the existence of two varieties.

Analytical Characters of a Mixture of Barium, Strontium, and Calcium Salts.—H. Baubigny.

Non-Existence of the Mixed Anhydrides.—L. Rousset.—When proceeding on the usual method the author has obtained merely a mixture of two anhydrides. This was found to be the case with the alleged acetylbutyric, acetyl-valerianic, and acetyl-benzoic acids.

Action of the Asymmetric Ketonic Compounds upon the Primary Aromatic Amines.—Louis Simon.—In the action of pyruvic acid upon a primary aromatic amine, there are formed simultaneously several compounds, but they are neither stereoisomers nor even structural isomers.

Action of the Chlorides of Acids upon Hexachlorophenol- α in presence of Aluminium Chloride. Formation of Ethers of Pentachlorophenol.—E. Barral.

Action of Aluminium Chloride on α -Hexachlorophenol.—E. Barral.—These two memoirs are not adapted for useful abstraction.

On Piperonylidene-acetone.—L. Rousset.—If 20 grms. of pure piperonal, regenerated from its bisulphite, are dissolved in 50 grms. dimethylketone, and if to this solution there are added 500 grms. water and 50 grms. soda at 10 per cent, on stirring the mixture heats, and there is produced a light yellow precipitate. This precipitate, if re-crystallised from alcohol, forms the compound in question.

Compound of Hexamethyleneamine with Bismuth Iodide.—M. Delépine.—This compound contains—Bismuth, 16.83; iodine, 58.24; nitrogen, 7.35; and water, 5.82 per cent.

On Hexamethyleneamine. (Further Continuation).—M. Delépine.—An account of the salts of the ammo-

niums:—The iodamylate, the action of acids, and the formation of primary amines.

On Hexamethyleneamine. (A Continuation).—M. Delépine.—The author describes here the solubilities, the hydrate, bromide, sulphate, and phosphate.

Oxidising Power of Laccase.—G. Bertrand.—The author has obtained from the latex of the lac tree of Tonkin a new soluble ferment, which he names laccase. This new ferment has the specific character of setting up the direct oxidation of the substances upon which it acts. It is thus distinguished from all the ferments previously known which occasion merely hydration and splitting up. The results cannot be ascribed to the action of micro-organisms, as the media in which the experiments were conducted were antiseptic.

Watering Milk. Its Detection by an Examination of the Whey.—H. Lescœur.—Every sample of milk which gives a serum of specific gravity below 1.027, and the solid matter of which does not amount to 67 grms. per litre, may be declared as "watered."

DEPARTMENT OF SCIENCE AND ART.

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THE CHEMICAL NEWS.

VOL. LXXII., No. 1867.

(STUDENTS' NUMBER).

ADDRESS TO STUDENTS.

PERHAPS a majority of the students to whom we venture to address our annual remarks look forward to the utilisation of the knowledge they are acquiring in some art or manufacture with which they hope to be specially connected; but there are others—too many we fear—who regard chemistry as the basis of an independent profession. Such men, in Britain, labour under the inconvenience of having as a body no recognised and distinctive name. In France they would be known as "Chemistes," and in Germany as "Chemiker," but the English equivalent of these terms has been in our country appropriated by the profession who are more suitably known in France as "Pharmaciens" and in Germany as "Apotheker," but who, with us, show no disposition to abandon the name of chemists. Nay, if "Tom Brown's" exposition of the law be correct, even such qualified designations as "analytical chemist" are the exclusive property of the compounders and dispensers of medicines. Some suggest the name "Analysts," which, however, connotes only a portion of the functions of the profession whose cause we are pleading. Professor Huxley, were he still living, might perchance have invented for us an unobjectionable name, which for the present must be allowed to stand over as a desideratum.

Concerning the relative rank of the profession our esteemed contemporary the *Chemiker Zeitung* is much exercised. It contends that if all chemists before being entitled to exercise their profession were obliged to pass a "Staat's examen," after their University career, they would no longer be regarded as inferior (!) to engineers and lawyers. What effect such an examination might have upon German public opinion we cannot presume to decide. But in the opinion of the world German chemists rank incomparably higher than any lawyers or engineers. No names among the latter classes carry with them the spell which adheres to the names of Liebig, Wöhler, Bunsen, or Hofmann. We are painfully conscious that in Britain, as no doubt also in Germany, the emoluments of the lawyer and of the engineer exceed those of the chemist. With us neither the engineer nor the chemist is a State-official. The latter is indeed relatively poor, since when he gives advice, whether to a private firm or to a public body, he is not paid by a percentage on the outlay which his schemes necessitate. Could he claim a percentage on the economy which he renders possible, he would be a more prosperous man than he is at present. Moreover, he is beset with difficulties to which, e.g., the engineer and the lawyer are strangers. He is, if we may use the expression, trespassed upon in all possible directions. As an instance, the difference between pure water and contaminated water is purely chemical and micro-biological. Only the chemist and the micro-biologist can appreciate such difference, can know

how to encounter it, and can judge if and in how far the methods used are successful. Yet, when the treatment of the sewage of London was under discussion, it was actually suggested that the engineer who had designed the Forth bridge—a matter purely mechanical—should be consulted! Why, had he even succeeded in building a railway across the Straits of Dover, that fact would have been no evidence of his power of purifying a single gallon of sewage. It is a strange thing that the Rivers' Pollution Commission included only one chemist to two engineers, and no microscopist or physician. In a very like manner, when question arises before any municipal body concerning the treatment of polluted waters, it is forthwith proposed to consult some eminent engineer.

But the chemist fares almost as badly at the hands of the legislature and its officials as does the experimental physiologist. The ukase ordering the addition of coal-naphtha to methylated spirits still exists, and causes a great hindrance to scientific research. The addition of a mere trace of Dippel's animal oil—as it is sanctioned by the German law—would have rendered the spirit more thoroughly undrinkable, without inflicting such annoyance on the chemical manufacturer and the scientist engaged in research. It further appears that a chemist is, strictly speaking, liable to a tax on every retort, &c., in his laboratory, of what material soever, and however incapable of being used for the illicit distillation of spirits.

Further, there is a chronic agitation kept up by some medical men (especially medical officers of health) and by a few pharmacists, to encumber the sale of the ordinary mineral acids with red-tape precautions. Any such enactment cannot have other than an unfavourable action upon chemical research. "Free research" should be the watchword of every man of Science, and it is in the long run essential to the welfare of the community.

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

CANDIDATES for any Degree in this University must have passed the Matriculation Examination. No exemption from this rule is allowed on account of Degrees obtained or Examinations passed at any other University. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, and Medals depending upon them, are open to Women upon exactly the same conditions as to Men.

There are two Examinations for Matriculation in each year; one commencing on the second Monday in January, and the other on the second Monday in June.

The Examination is conducted by means of Printed Papers; but the Examiners are not precluded from putting, for the purpose of ascertaining the competence of the candidates to pass, *viva voce* questions to any candidate in the subjects in which they are appointed to examine. These Examinations may be held not only at the University of London, but also, under special arrangement, in other parts of the United Kingdom, or in the Colonies.

Every candidate for the Matriculation Examination must, not less than five weeks before the commencement of the Examination, apply to the Registrar for a Form of Entry, which must be returned not less than four weeks before the commencement of the Examination, accompanied by a Certificate showing that the candidate has completed his sixteenth year, and by his Fee for the Examination.

As no candidate can be admitted after the List is closed, any candidate who may not have received a Form of Entry within a week after applying for it must communicate immediately with the Registrar, stating the exact date of his application and the place where it was posted.

Every candidate entering for the Matriculation Examination for the first time must pay a Fee of £2 to the Registrar. If a candidate withdraws his name, or fails to present himself at the Examination, or fails to pass it, the Fee shall not be returned to him, but he shall be allowed to enter for any subsequent Matriculation Examination upon payment, at every such entry, of an additional Fee of £1, provided that he comply with the Regulations in the preceding paragraph.

Candidates are not approved by the Examiners unless they have shown a competent knowledge in each of the following subjects:—Latin. Any one of the following Languages:—Greek, French, German, Sanskrit, or Arabic. The English Language, and English History, with the Geography relating thereto. Mathematics. Mechanics. One of the following branches of Science:—Chemistry, Heat and Light, Magnetism and Electricity, Botany.

The Examination in Chemistry is—Chemistry of the Non-metallic Elements; including their compounds, their chief physical and chemical characters, their preparation, and their characteristic tests.

A Pass Certificate, signed by the Registrar, will be delivered to each successful candidate after the Report of the Examiners has been approved by the Senate.

If in the opinion of the Examiners any candidates in the Honours Division of not more than twenty years of age at the commencement of the Examination possess sufficient merit, the first six among such candidates will receive an Exhibition of thirty pounds per annum for the next two years; the second among such candidates will receive an Exhibition of twenty pounds per annum for the next two years; and the third will receive an Exhibition of fifteen pounds per annum for the next two years; such exhibitions are payable in quarterly instalments provided that on receiving each instalment the Exhibitor declares his intention of presenting himself either at the two Examinations for B.A., or at the two Examinations for B.Sc., or at the Intermediate Examination in Laws, or at the Preliminary Scientific M.B. Examination, and Intermediate Examination in Medicine, within three academical years from the time of his passing the Matriculation Examination.

Under the same circumstances, the fourth among such Candidates will receive a prize to the value of ten pounds in books, philosophical instruments, or money; and the fifth and sixth will each receive a prize to the value of five pounds in books, philosophical instruments, or money.

Any candidate who may obtain a place in the Honours Division at the Matriculation Examination in January is admissible to the Intermediate Examination either in Arts or in Science in the following July.

INTERMEDIATE EXAMINATION IN SCIENCE.

The Intermediate Examination in Science will commence on the third Monday in July.

No candidate (with the exception of such as have obtained Honours at the Matriculation Examination in the preceding January) is admitted to this Examination within one academical year of the time of his passing the Matriculation Examination.

The Fee for this Examination is £5.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. In addition, they will be examined practically in Simple Qualitative Analysis. This Examination will consist of six hours' examination by two printed papers and of six hours' practical work.

In the Examination for Honours, the Candidate, not

being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.Sc. EXAMINATION.

The B.Sc. Examination will be held on the third Monday in October.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously.

The Fee for this Examination is £5.

Examination for Honours.

The examination for Honours in Chemistry will take place on Monday, Tuesday, and Wednesday in the week following the Examination for Honours in Mathematics; on Monday by printed papers (chiefly on Organic Chemistry), and on Tuesday and Wednesday by practical examination in Qualitative and Quantitative Analysis.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

DOCTOR OF SCIENCE.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

Every candidate for this Degree must state in writing the special subject within the purview of the Faculty of Science, as set out in the Programme of the B.Sc. Examination, upon a knowledge of which he rests his qualification for the Doctorate; and with this statement he shall transmit an original Dissertation or Thesis (at least six copies), printed, type-written, or published in his own name, treating scientifically some special portion of the subject so stated, embodying the result of independent research, or showing evidence of his own work, whether conducted independently or under advice, and whether based on the discovery of new facts observed by himself, or of new relations of facts observed by others, or, generally, tending to the advancement of Science. Every candidate may further specify any printed contribution or contributions to the advancement of Science which he has at any time previously published. If the Dissertation or Thesis be approved by the Examiners, the candidate shall be required to present himself at the University upon such day or days within the first twenty-one days of June as may be notified to him, and shall, at the discretion of the Examiners, be further tested, either orally or practically, or by printed questions or by all of these methods, with reference both to the special subject selected by him and to the Thesis.

PRELIMINARY SCIENTIFIC (M.B.) EXAMINATION.*

This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the third Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

No candidate shall be admitted to this Examination unless he shall have passed the Matriculation Examination. Not less than five weeks before the commencement of the Examination he must apply to the Registrar for a Form of Entry, which must be returned not less than four weeks before the Examination, accompanied with the candidate's fee.

The Fee for this examination is Five Pounds.

* Candidates who pass in all the subjects of the Preliminary Scientific (M.B.) Examination, and also pass at the same time in the Pure and Mixed Mathematics of the Intermediate Examination in Science, or who have previously passed the Intermediate Examination in Arts, are admissible to the B.Sc. Examination.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry.—W. Odling, M.A., F.R.S.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years, passing at least two examinations in Arts, and one in either Mathematics, Natural Science, Law, Modern History, or Theology, when, if he obtain a first, second, or third class, he can take his B.A. Degree; if he do not gain such honour he has to pass a third examination in *Literis Humanioribus*.

The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

Scholarships of about the value of £75 are obtainable at Christ Church, Magdalen, and other colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the University Calendar; the Examination Statutes, 1894; the Student's Handbook to the University; and from the professors.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry.—G. D. Liveing, M.A., F.R.S.
Jacksonian Professor of Natural and Experimental Philosophy.—J. Dewar, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in the first or third term of residence, or, through the Oxford and Cambridge Schools Examination Board, or through the Senior Local Examinations, before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

The scholarships, ranging in value from £20 to £100 a year, are chiefly given for mathematical and classical proficiency. Scholarships, or Exhibitions, are given for Natural Science in King's, Trinity, St. John's, St. Peter's, Clare, Trinity Hall, Queen's, Jesus, Christ's, Sidney, Pembroke, Caius, and Downing Colleges; the examinations being in December, at Easter, and in June and October.

The Chemical Laboratory of the University is open daily for the use of the Students. The Demonstrators attend daily to give instructions. A list of the lectures is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrar, Cambridge, or from the *Cambridge University Calendar*.

UNIVERSITY OF DUBLIN.

TRINITY COLLEGE.

Professor of Chemistry.—J. Emerson Reynolds, D.Sc., M.D., F.R.S.

Assistant Lecturer.—Emil A. Werner, F.C.S., F.I.C.

Demonstrator.—William Early, F.I.C.

The general Laboratories include working accommodation for 120 Students, and the Quantitative and Research Laboratories for about 40 Students. The Laboratories will open on the 1st of October. Lectures will commence about November 1st.

The Laboratories and the Lectures of the Professor of Chemistry can now be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry

occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The following Lectures are delivered:—

1. *Inorganic Chemistry and Chemical Philosophy.*—Elementary, first year; advanced, second year.
2. *Organic Chemistry.*—General, second year; advanced, third year.
3. *Metallurgy.*—A Course for Engineering and Technical Students.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The *Summer Course of Practical Chemistry for Medical Students* begins during the first week in April and terminates with the first week in July.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

KING'S COLLEGE.

(DIVISION OF ENGINEERING AND APPLIED SCIENCE).

Professor of Chemistry.—J. M. Thomson, F.R.S.E., F.C.S.

Demonstrator of Practical Chemistry.—Herbert Jackson, F.C.S.

Assistant Demonstrators.—P. H. Kirkaldy and W. H. Sodeau.

Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a View of the Forces which concur to the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic Elements and their principal compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated. Examinations of the Class, both *visd voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, and they go through a course of Manipulation in the most important operations of Chemistry, including the first steps of Analysis. Any Student of this Division may be admitted to this Class at any period of his study on payment of an extra fee.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday, on which day the hours are from ten till one.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Special hours and fees are arranged for the convenience of such Third Year Students as wish to study Analytical Chemistry.

Fees.—Chemistry per term, £3 3s. od.; per ann., £8 8s. od.; Practical Chemistry per term, £4 4s. od.; per ann., £10 10s. od.; Experimental and Analytical Chemistry—Daily attendance: One month, £4 4s.; Three months, £10 10s.; Six months, £18 18s.; Nine months, £26 5s. Three days a week: One month, £2 12s. 6d.; Three mos., £6 6s.; Six mos., £11 11s.; Nine mos., £15 15s.

Rules as to Admission of Students.

1. The Academical Year consists of Three terms: Michaelmas Term, from beginning of October to the week

before Christmas; Lent Term, from the middle of January to the week before Easter; Easter Term, from Easter to the beginning of July.

II. The days fixed for the Admission of New Students: in the Academical Year 1895-96, are Tuesday, October 1, Wednesday, January 15, and Wednesday, April 22.

METALLURGY.

Professor.—A. K. Huntington, F.I.C., F.C.S., &c.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is paid to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery.

PHOTOGRAPHY.

Lecturer.—Prof. J. M. Thomson, F.R.S.E., F.C.S.

Arrangements are made for a complete Course of Instruction in Photography to the students of the third year. A glass house has been erected, and in connection with it a Laboratory for the preparation of Photographic Chemicals. Students entering to this department will be afforded every facility for practising the Art in all its branches.

In addition to the regular College Course in Photography occasional classes are formed, consisting each of about six gentlemen, who meet twice a week. The fee for private instruction is £5 5s. for ten lessons, or £10 10s. for three courses. There is in every case a charge of £1 each course for chemicals.

EVENING CLASSES.

Classes for Evening Instruction in various subjects are held during the months from October to March, inclusive, and during the months of April, May, and June.

UNIVERSITY COLLEGE.

FACULTY OF SCIENCE.

Professor.—William Ramsay, Ph.D., F.R.S.

Assistant Professor.—J. N. Collie, Ph.D.

Assistants.—Morris Travers, B.Sc., and N. T. M. Wilsmore, M.Sc.

The Session is divided into three Terms, as follows, all the dates being inclusive:—

First Term, from Wednesday, October 2nd, until Friday, December 20th;

Second Term, from Tuesday, January 14th, 1896, till Friday, March 27th;

Third Term, from Tuesday, April 21st, till Wednesday, July 1st. Class Examinations begin on June 18th.

Junior Courses.

First Term: Tuesday and Thursday at 11, and Saturday at 10. Third Term: Tuesday and Thursday at 10, Friday at 4. Fee:—£4 4s.

These Courses will each consist of about thirty lessons, partly theoretical and partly practical, on the non-metallic elements. Frequent exercises will be given.

Senior Course of Chemistry.

First and Second Terms: The Class meets four times a week, on Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises.

Fee:—For the Course, £7 7s.; Perpetual, £9 9s.; for the First or Second Terms, £4 4s.

This Course and the Practical Class cover the subject as prescribed for the Preliminary Scientific (M.B.) and Int. Examination in Science of the University of London.

For the Preliminary Scientific Examination Students who take the three subjects for that examination in July attend during the First and Second Terms.

Advanced Course of Chemistry.

Second and Third Terms.—The class meets twice a week, on Tuesdays and Thursdays, at 9, beginning on January 14. The hour will be altered by special arrangement with the class if necessary.

Fee:—For the Course, £3 3s.; for a Term, £2 2s.

This Course will be found suitable for those about to proceed to graduation as Bachelor of Science in London University, and to those who intend to choose Chemistry as a profession. Such students should also work in the Laboratory during as many hours as they can spare.

Organic Chemistry.

Tuesday and Thursday, at 9, in the First Term; Tuesday, Thursday, and Saturday, at 10, in the Second Term; and Tuesday and Thursday at 9, and Saturday at 11, in the Third Term. The hour of meeting will be altered should the class desire it.

This Course of Organic Chemistry is intended for those who in studying the subject have not a Medical Examination chiefly in view. Candidates for Honours at the Int. M.B. are, however, recommended to attend this Course instead of the Special Summer Course.

The Course includes the subjects required at the B.Sc. Examination, Pass and Honours; but no previous acquaintance with Organic Chemistry will be expected of those joining the Class.

Fee:—For the Course, £6 6s.; for the Second and Third Terms, £4 14s. 6d.; for a Term, £2 12s. 6d.; for a Second Course, £3 3s.

Practical Class.

First and Second Terms, Tuesday and Thursday, at 11.

Fee, including cost of materials, £5 5s.; for a Second Course, £3 3s.

The Course includes the Practical Chemistry required at the Preliminary Scientific and Intermediate Science Examinations.

Senior Practical Class.

Wednesdays from 2 to 4 and Saturdays from 10 to 12 during the Third Term; also Tuesdays and Thursdays from 11 to 12.

Fee:—(Including cost of materials) £5 5s.; for a Second Course, £3 3s.

Analytical and Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

The Laboratory Course includes the Practical Chemistry required at the following Examinations of the University of London:—Prel. Sci. (M.B.), Intermediate M.B., Intermediate Science, B.Sc.

Students who wish to attend the Lectures on Chemical Technology may acquire here the requisite knowledge of Practical Chemistry and Analysis.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Course qualifies Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent Students on the work done during the Session. The Tuffnell Scholarship (£100 for two years) will also be competed for in the Session 1895-96; also the Cloth-worker's Scholarship of £30.

ROYAL COLLEGE OF SCIENCE AND
ROYAL SCHOOL OF MINES.

Professor.—W. A. Tilden, D.Sc., F.R.S.

Assistant Professor.—W. P. Wynne, D.Sc., A.R.C.S.

Demonstrators.—H. Chapman Jones and J. W. Rodger, A.R.C.S.

Assistants.—G. S. Newth, W. Tate, A.R.C.S., and A. Eiloart, Ph.D., D.Sc.

The Royal College of Science at South Kensington is intended, primarily, for the instruction of teachers, and of students of the industrial classes selected by competition in the examinations of the Science and Art Department. The Royal School of Mines is incorporated with the Royal College of Science. Students entering for the Associateship of the Royal School of Mines obtain their general scientific training in the Royal College of Science. The instruction in the Royal College of Science is arranged in such a manner as to give the Students a thorough training in the general principles of Science, followed by advanced instruction in one or more special branches of Science. The Associateship is granted in certain divisions or lines of study. Students who go through any one of the prescribed courses of instruction and pass the necessary Examinations receive a Certificate of Associateship of the Royal College of Science, or of the Royal School of Mines. Students who are not candidates for the Associateship are permitted to enter as occasional students in one or more special branches of science, and on passing the examination receive a Certificate to that effect. The Associateship of the Royal College of Science is given in one or more of the following divisions:—Mechanics, Physics, Chemistry, Biology, Geology, and Agriculture, and the Associateship of the Royal School of Mines in Metallurgy and Mining.

The course of instruction, which lasts for three years, is the same for all the divisions during the first year, after which it is specialised in accordance with the Scheme detailed in the Prospectus of the School.

The Session is divided into two Terms. The first Term begins on the 2nd of October and ends about the middle of February. The second Term begins in the middle of February and ends about the middle of June.

Examinations are held at the end of each course of instruction and at such other periods as may be found necessary. On the results of these examinations the successful candidates are arranged in two classes, first and second. There are also "Honours" examinations for the subjects of the third year, the successful candidates being placed in order of merit. A student obtains the Associateship who passes in all the subjects of the first two years and in the third year those of the special division he selects for his Associateship. A student who goes through the prescribed course of instruction in any subject and passes the final examination in it receives a certificate to that effect.

Students who do not wish to attend the lectures are admitted for short periods to the laboratories, at the discretion of the Professors. The fees for the laboratories are £4 per month.

Students not entering for the Associateship are admitted to any particular course of study, so far as there is room, on payment of the fees shown in the following table:—

	Lectures.	Laboratory.
Chemistry	3	13
Physics	5	12
Biology with Botany .. .	5	12
Geology with Mineralogy ..	4	8
Mechanics	4	6
Metallurgy	2	13
Mining	4	
Astronomical Physics .. .	2	3

Agricultural Chemistry, per term, £13. Mathematics and Mechanical Drawing, £3 per term. Model and Free-hand Drawing, £1 per term. Descriptive Geometry, £3 per session. Mine Surveying, £10.

The fees for the first two years amount to about £75, and for the remainder of the course for the Associateship they vary from £30 to about £40.

Both the private and the State-aided students are required to furnish themselves with certain instruments and apparatus before the commencement of the courses. These are enumerated in the syllabuses of the several subjects.

Officers of the Army, Navy, and Civil Service, recommended by their respective Departments, are admitted to the Lectures and Laboratories at half fees.

Associates of the Royal College of Science or of the Royal School of Mines have the privilege of free admission to the Library and to all the courses of lectures.

Bona fide teachers qualified to earn payments for teaching Science according to the rule of the Science and Art Directory may obtain permission to attend free any course of lectures.

Several valuable Exhibitions, Scholarships, and Prizes are attached to the studentship.

Summer Courses for Teachers.—Short courses of instruction are given annually, about July, in different branches of science for the benefit of teachers of science schools in the country. The courses last three weeks. About 250 teachers are admitted to them, and they receive third class railway fare to and from South Kensington, and a bonus towards their incidental expenses of £3 each. (See Science and Art Directory.)

Working Men's Lectures.—Notification of these will be given in the newspapers.

THE SCHOOL OF THE
PHARMACEUTICAL SOCIETY OF GREAT
BRITAIN.

The Fifty-fourth Session will commence on Wednesday, October 2nd, 1895. Entries not previously arranged with the Dean or Secretary may be made between 10 a.m. and 1 p.m. on that day.

Professors and Lecturers.—Prof. Dunstan, M.A., F.R.S., Sec. C.S., F.I.C., Chemistry; Prof. Attfield, Ph.D., F.R.S., F.I.C., Practical Chemistry; Prof. Green, Sc.D., F.R.S., F.L.S., Botany (Dean); Prof. Greenish, F.I.C., F.L.S., Materia Medica; Mr. Joseph Ince, F.L.S., Pharmacy and Practical Pharmacy.

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry commences in October and terminates at the end of March. An Advanced Course of Lectures on Organic Chemistry begins in April and extends to the end of June. The lectures will be given at 9.30 a.m. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. A bench in the chemical laboratories, which are open daily throughout the Session, can be engaged for any period. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies.

Prospectuses and further information may be obtained from Mr. Ernest J. Eastes, F.I.C., Secretary to the School, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES,
ABERYSTWYTH.
UNIVERSITY OF WALES.

Professor.—H. Ll. Snape, D.Sc. (Lond.), Ph.D. (Göttingen), F.I.C.

Assistant Lecturer and Demonstrator.—A. W. Warrington, M.Sc. (Vic.), F.I.C.

Assistant Lecturer in Agricultural Chemistry.—J. Alan Murray, B.Sc. (Edin.).

The College is open to male and female students above the age of sixteen years. The Session commences on Monday, September 30, on which day all Students will be expected to meet the Professors in the Library of the College.

Lecture Courses.—(1) Matriculation Course; three lectures weekly during the Michaelmas and two weekly during the Lent and Easter Terms. (2) Intermediate Science Pass Course; four lectures weekly during the Lent and Easter Terms. (3) Intermediate Science Honours Course; two lectures weekly during the Lent and Easter Terms. (4) B.Sc. Course; three lectures weekly throughout the Session. (5 and 6) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 lectures weekly throughout the Session.

Laboratory Courses.—The Laboratory is open daily from 10 a.m. to 1 p.m., and from 2.15 to 5 p.m., except on Saturdays. Classes for the Systematic Study of Qualitative and Quantitative Analysis will be formed, and Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland, and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spent at Aberystwyth.

Fees.—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 10s. per term, and for twelve hours, 20s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 17, and exhibitions are awarded at the end of the Session on the results of the class examinations.

The Chemical Laboratories in connection with this College have been recently built, and are fitted with every convenience for the prosecution of chemical studies.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Prospectuses issued for the Agricultural and Normal Departments.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

Chemistry.—Professor, James J. Dobbie, M.A., D.Sc. Demonstrator, Fred. Marsden, Ph.D., B.Sc. Assistant Lecturer in Agricultural Chemistry, F. V. Dutton.

Physics.—Professor, Andrew Gray, M.A., F.R.S.E. The Session opens October 2nd, 1895. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Matriculation Course.—Subjects: Those prescribed for the London University Matriculation Examination. Fee for the Term £2 2s. A class for revision of Matriculation Work will be held during the Summer Term. Fee for the Term, £1 1s.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Term £2 2s.

B.Sc. Course.—Organic Chemistry. Fee for the Session, £3 3s.

Medical Course.—Inorganic and Organic Chemistry. Fee for the whole Course, £4 4s.

Agricultural Chemistry.—Fee, £2 2s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 4 p.m. for instruction in Chemical Analysis and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s.; twenty-four hours, £4 4s. Composition Fee for all Laboratory Classes of the Intermediate Science Course taken in one year, £4 4s.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and students can make one *Annus medicus* at the college. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE, CARDIFF.

Professor.—C. M. Thompson, M.A., D.Sc., F.C.S.

Demonstrators.—E. P. Perman, D.Sc., F.C.S., and A. A. Read, F.I.C., F.C.S.

The Session commences October 7th, and terminates on June 26th, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 50 lectures, and will cover the subjects prescribed for the Matriculation examinations of the University of Wales and the University of London. Fee, £2 2s. A revision class is held in the Summer term.

The Intermediate Course consists of about 80 lectures held during the Lent and Summer terms in continuation of the Junior Course, and is the qualifying course for the Intermediate Examination of the University of Wales. Together with laboratory practice, it will cover the subjects required for the Intermediate Examination in Science and the Prel. Sci. (M.B.) Examination of the University of London. Fee, £4 4s.

The Senior Course consists of some 90 lectures devoted to Organic Chemistry; Fee, £3 3s.

A course of 20 lectures on Qualitative Analysis will also be given.

The following lectures on Metallurgy will be given by Mr. Read:—10 lectures on Fuel; Fee, 10s. 6d. 20 lectures on General Metallurgy; Fee, £1 1s. 30 lectures on the Manufacture of Iron and Steel; Fee, £1 1s. A practical course on Iron and Steel Analysis will also be held.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £3 3s. per session; twelve hours, £2 2s. per term; eighteen hours, £3 3s. per term; twenty-four hours £4 4s. per term.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students wishing to graduate at a Scottish University, or preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

The College is recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of London

may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in September, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospects and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Women Students is attached to the College.

UNIVERSITY COLLEGE, BRISTOL.

Professor of Chemistry.—Sydney Young, D.Sc., F.R.S.
Lecturer.—Arthur Richardson, Ph.D.

The session 1895-96 will begin on October 4th. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratory. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the College into their offices and workshops as articulated pupils at reduced terms. Medical education is provided by the Faculty of Medicine of the College. Several Scholarships are tenable at the College. Full information may be obtained from the Secretary.

DAY LECTURES.

Inorganic Chemistry.

The Courses treat of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

Junior Course.—Two Lectures a week will be given during the First and Second Terms.

Senior Course.—Three Lectures a week will be given throughout the Session.

Advanced Course.—One Lecture a week will be given throughout the Session.

Organic Chemistry.

This Course will relate to the more important groups of the Compounds of Carbon.

Two Lectures a week will be given during the Second Term, and three Lectures a week during the Third Term. Fee, £3 3s. An advanced course of lectures will also be given one day a week during the session.

Practical Chemistry.—Laboratory Instruction.

The Laboratory will be open daily from 10 a.m. to 5 p.m., except on Saturdays, when it will be closed. Instruction will be given in the Laboratory in all branches of Practical Chemistry, including Qualitative and Quantitative Inorganic and Organic Analysis, the preparation of Chemical Products, and Inorganic and Organic Research. Special facilities will be afforded to those who desire to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures. The Laboratory is under the immediate supervision of the Professor and the Lecturer. Fees in Guineas—

	5 Days a Week.	4 Days a Week.	3 Days a Week.	2 Days a Week.	1 Day a Week.
Per Session ..	15	12½	10	7½	5
„ Two Terms ..	11	9	7½	5½	3½
„ One Term ..	7	6	4½	3½	2½

Students may arrange to divide their days of laboratory work into half-days.

Chemical Scholarship.—Among others, a Chemical Scholarship of £25 is offered for competition.

EVENING LECTURES.

Two courses of Lectures will be delivered during the First and Second Terms; they will be devoted to the consideration of the general Principles of Chemistry and Chemical Physics and the Chemistry of Non-Metallic and Metallic Elements. Special attention will be paid throughout to those products which have a practical application in the Arts and Manufactures. Fee for each course, 7s. 6d.

University College, Bristol, has been approved by the Council of the Institute of Chemistry as a College at which all the subjects required for the admission of Associates to the Institute are taught.

MASON COLLEGE, BIRMINGHAM.

Professor.—Percy F. Frankland, Ph.D., B.Sc., F.R.S.

Assistant Lecturer.—C. F. Baker, Ph.D., B.Sc.

Demonstrator.—D. R. Boyd, B.Sc.

The Session will be opened on October 1st, 1895.

Elementary Course.

Forty Lectures adapted to the requirements of beginners will be given in the Winter and Spring Terms. Lecture days—Wednesdays and Fridays at 11.30.

Persons entirely unacquainted with Chemistry are recommended to attend this Course before entering for the General Course. Candidates for the Matriculation Examination of the University of London also are advised to attend this Course.

General Course.

The General Course of Lectures on Chemistry will be found useful by Students who are afterwards to become Engineers, Architects, Builders, Brewers, or Manufacturers (such as Metallurgists, Alkali, Soap, Manure, Glass, or Cement Makers, Bleachers and Dyers, &c.)

Students preparing for the Intermediate Examination in Science and Preliminary Scientific (M.B.) Examination of the University of London should attend the Lectures on Inorganic Chemistry (Winter and Spring Terms).

Candidates for Intermediate Examinations in Medicine will in general require only that part of the course (Summer Term) which relates to Organic Chemistry.

The full course, extending over three terms, will also satisfy the requirements of Students preparing for the Associateship of the Institute of Chemistry, so far as attendance at lectures on General and Theoretical Chemistry is concerned.

1. From October to March (Winter and Spring Terms). About eighty lectures on Inorganic Chemistry and Chemical Philosophy will be given on Mondays, Tuesdays, Wednesdays, and Thursdays from October to December, and on Mondays, Tuesdays, and Wednesdays from January to March, at 9.30 a.m. A Tutorial Class is held in connection with this Course once a week throughout the Session. Fee, £5 5s. for the course.

2. May to July (Summer Term). About thirty lectures will be given on Elementary Organic Chemistry, or the chemistry of the most important series of carbon compounds. This course will include all the subjects required for the Intermediate Examination in Medicine of the University of London. Lecture Days—Monday, Wednesday, and Friday at 11.30 a.m. Fee, £1 11s. 6d.

The General Course (including Inorganic and Organic lectures) qualifies for graduation in the medical faculties of the universities of Edinburgh, Glasgow, Aberdeen, and Durham.

Advanced Course.

An Advanced Course for the study of Theoretical Chemistry and those parts of the subject which are required for the degree of B.Sc. in the University of London will meet twice a week. Fee for the session £3 3s.

Laboratory Practice.

The College Laboratory is open daily from 9.30 to 5, except on Saturdays, when it is closed at 1 p.m.

Candidates for Intermediate Examination in Science, Preliminary Scientific (M.B.), B.Sc., and Intermediate Examination in Medicine of the University of London, may obtain in the Laboratory of the College the instruction necessary. The three months Course of Practical Chemistry for the B.Sc., Edinburgh, in the department of Public Health, may be taken in the Mason College Laboratory. Fees:—

	All day.	Three hours per day.
One Term	7 guineas	4½ guineas.
Two Terms	13 "	8½ "
Three Terms	18 "	12 "

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Metallurgy.

Three Courses of Ten Lectures will be given on the Principles and Practice of Metallurgy. Fee, 10s. 6d. for each of the first two courses, and for each of the two sections of the third course. A more advanced course of about sixty lectures upon selected subjects is also given by Mr. McMillan, the Lecturer in Metallurgy.

There is a separate laboratory for metallurgical students in which provision is made for instruction in assaying, &c.

Evening Classes.

Several Courses of Evening Lectures are arranged during the Winter and Spring Terms of each session. The subjects are treated in a less technical manner and the fees are nominal.

Scholarships.

Priestley Scholarships.—Three Open Scholarships in Chemistry of the value of £100 each are awarded annually in September.

Bowen Scholarship.—One Open Scholarship in Metallurgy of the value of £100 is awarded annually in September.

Forster Research Scholarship.—A Scholarship of the value of £50 is annually awarded.

For particulars apply to the Registrar.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor or Lecturer.

BRADFORD TECHNICAL COLLEGE.

CHEMISTRY AND DYEING DEPARTMENT.

Professor.—(Vacant).

Demonstrator.—(Vacant).

Lecturer on Botany and Materia Medica.—William West, F.L.S.

The school year is divided into three terms. The Session commences on September 16th and terminates on July 22nd. The course of instruction extends over two years, and embraces Lecture Courses on Inorganic and Organic Chemistry, the technology of the textile fibres, mordants, natural and artificial colouring matters, technical analysis, and laboratory practice in analytical chemistry, chemical preparations, and dyeing. Inclusive fee, £4 4s. per term.

During the first and second terms Evening Classes are held for the benefit of persons engaged during the day and for pharmaceutical students.

ROYAL AGRICULTURAL COLLEGE,
CIRENCESTER.

CHEMICAL DEPARTMENT.

Professor.—Prof. E. Kinch, F.C.S., F.I.C.

Assistants.—Cecil C. Duncan, F.I.C., and W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation and stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

VICTORIA UNIVERSITY.

THE YORKSHIRE COLLEGE, LEEDS.

Professor of Chemistry.—Arthur Smithells, B.Sc. Lond., F.I.C.

Lecturer in Organic Chemistry.—Julius B. Cohen, Ph.D., F.I.C.

Assistant Lecturer in Agricultural Chemistry.—Herbert Ingle, F.I.C.

Demonstrators.—A. C. Wright, B.A., and T. Ewan, Ph.D., B.Sc.

The Session begins October 8, 1895.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday and Friday, at 11.30 a.m., from October to the end of the second term, and during part of the third term. Fee for the Course, £4 4s.
2. Inorganic Chemistry.—First year Honours Course, Non-metals. Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £3 13s. 6d.
3. Inorganic Chemistry.—Second year Honours Course, Metals. Tuesday, Thursday, and Saturday at 9.30 a.m. Fee, £3 13s. 6d.
4. Organic Chemistry.—Tuesday, Thursday, and Saturday at 12 noon. Fee £3 13s. 6d.
5. Organic Chemistry Honours Course.—Wednesday and Friday at 12 noon. Fee, £2 12s. 6d.
6. Theoretical Chemistry.—Advanced Course. Tuesdays and Thursdays at 9.30 a.m. Fee, £2 12s. 6d.
7. Chemistry as Applied to Coal Mining.—Tuesday during the First Term, at 4 p.m.
8. Agricultural Chemistry.—Monday, Tuesday, and Friday, at 3 p.m., during first and second terms.
9. Chemistry for Teachers.—Saturdays from 9.30 to 12.30 in the first and second terms. Fee, £4 4s.

Laboratory Courses.

The College Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session.—Students working six days per week, £21; five, £18 18s.; four, £16 16s.; three, £13 13s.

Class in Practical Chemistry. Saturday mornings, from 9.30 to 12.30. Fee £1 11s. 6d.

Practical Chemistry for Medical Students.—Tuesdays, 9.30 to 11.30 October to end of December; Thursdays, 2 to 4 from January to end of March.

Practical Course in Sanitary Chemistry.—At times to be arranged.

Practical Organic Chemistry for Medical Students.—At times to be arranged.

Evening Class.

A Course of twenty Lectures by Mr. Ingle, on the Chemistry of Combustion will begin during the first and second Terms, on Wednesdays, at 7.30 p.m., beginning October 10. Fee, 10s. 6d.

Dyeing Department.

Professor.—J. J. Hummel, F.I.C.

Lecturer and Research Assistant.—A. G. Perkin, F.R.S.E.

Assistant Lecturer.—W. M. Gardner.

This Course extends over a period of three years, and is intended for those who wish to obtain a full scientific and practical education in the art of dyeing. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, e.g., the sons of manufacturers, calico printers, managers, master dyers, &c.

Leather Industries Department.

Lecturer.—H. R. Procter, F.I.C.

The full Course, which extends over a period of three years, is suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and is recommended to sons of tanners. The Course includes instruction in chemistry, engineering, leather manufacture, and practical work in the Leather Industries Laboratory.

Agricultural Department.

Professor.—James Muir.

The full Course occupies two years, and includes instruction in chemistry, physics, botany, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out-door agriculture.

Research Students are admitted to the College Laboratories on reduced terms.

Several valuable Scholarships are at the disposal of the College, viz., the Cavendish, Salt, Akroyd, Brown, Emsley, Craven, and Clothworkers' Scholarships, and the Leighton Trustees' Exhibition, and one of the 1851 Exhibition Scholarships. The West Riding County Council Scholarships are tenable at the Yorkshire College.

UNIVERSITY COLLEGE, LIVERPOOL.

Professor.—J. Campbell Brown, D.Sc.

Lecturer on Organic Chemistry.—C. A. Kohn, B.Sc., Ph.D.

Lecturer on Metallurgy.—T. L. Bailey, Ph.D.

Demonstrators and Assistant Lecturers.—T. L. Bailey, Ph.D., C. A. Kohn, B.Sc., Ph.D., and S. B. Schryver, B.Sc., Ph.D.

Assistant.—H. H. Froyssell.

The Session commences October 3rd.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D.Sc. Degree in Victoria University; for Degrees in Medicine of Victoria, London, and Edinburgh; for a special Technological Certificate of University College; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry of Great Britain and Ireland, and other Examination Boards.

Lecture Courses.

General Elementary Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, £4.

Dental Course, Lectures and Practical. Fee, £3 5s.

Course A.—Non-metals. Fee, £3 10s.

Course B.—Metals. Fee, £3 10s.

Course C.—Organic Chemistry. Fee, £3 10s.

Course H.—Special Organic Subjects. Fee, £1.

Course D.—Physical Chemistry. One Term. Fee, £1.

Course E.—History of Chemistry and of the Development of Modern Chemical Philosophy. Three Terms. Fee, £2.

Courses F.—Technological Chemistry and Metallurgy: Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and Allied Manufactures. (2) Copper, Iron, and Steel. (3) Lead, Silver and Gold, Aluminium, and other Metals. (4) Distillation of Coal and Tar Industries. (5) Fuel and Gas. (6) Chemistry Applied to Sanitation. (7) Technical Gas Analysis. Three terms. Fee, each course £1 10s.

Practical Classes.

(1) Junior. (2) Intermediate: Qualitative Analysis of Inorganic Substances and of some of the more common Organic Substances. (3) Revision Class. (4) Senior: Practical Organic (Advanced Medical Class). (5) Practical Exercises on Technology, Pharmaceutical Chemistry, Saitanry subjects, Examination of Water and Air, of Animal Secretions, Urinary Deposits, Calculi, and Poisons. (6) Quantitative Class: Course arranged to suit the requirements of the London University B.Sc. Examinations, Pass and Honours, and for Intermediate M.B. Honours.

Chemical Laboratory.

The Chemical Laboratories provide accommodation for every kind of chemical work.

Additional metallurgy furnaces have been built, and a department for practical study of Electricity applied to Chemical Analysis has been added during the past year, and a large extension of the laboratories is in progress this year.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study.

TABLE OF FEES.

Per Week.	One Term, Three Months.	Three Terms, One Session.
One day	£4	£8
Two days	6	10
Three days	8	12
Four days	9	15
Whole week	10 10s.	21

Pharmaceutical Course, £11.

Technological Curriculum.

Preliminary Year.—Chemistry, the Elementary Course. Practical Classes 1 and 2. Mathematics, or Mechanics, or Physics. Elementary Engineering, Drawing, and Design (in this or one of the following years). German. Or the Victoria Preliminary Course and Examination may be taken.

First Year.—Chemistry—Courses A and B; Chemical Laboratory three days per week; Practical Organic Class during the Summer Term; Technological Chemistry, Course F. Physics, with laboratory work, one day per week. Mathematics (intermediate). German. Engineering, First Year Course, Autumn and Lent Terms. Intermediate B.Sc. Examination may be passed.

Second Year.—Chemistry, Lecture Course C, on Organic Chemistry, Lecture Course E or D, Technological Chemistry, Course F, on Metallurgy. Chemical Laboratory, four days per week. Engineering, Mathematics, or Physics (Advanced). The Final Examination for the Victoria B.Sc., or the Intermediate Examination of the Institute of Chemistry, may be taken.

Third Year.—Courses D, F, and C. Any other Courses omitted in a previous year. Laboratory, five days per week. Students may finally choose a special subject either of research or of applied Chemistry. The Final Examination for the Associateship of the

Institute of Chemistry of Great Britain and Ireland may be taken. Three years study after passing the Preliminary Examination of Victoria University are required for the B.Sc. Degree in the Honours School of Chemistry.

The Sheridan Muspratt Chemical Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1895, on an Examination in subjects which are included in the first two years of the above curriculum. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

Evening Classes.

Classes will be held on Metallurgy and on Analysis of Gases.

The Prospectus containing full particulars may be obtained from the Registrar, University College, Liverpool.

LIVERPOOL COLLEGE OF CHEMISTRY.

Principal.—George Tate, Ph.D., F.I.C., F.C.S.

The Laboratories are open daily from 10 to 5, excepting Saturdays, when they close at 1 p.m. The course of instruction is adapted to the requirements of students of Chemistry as a science, and in its applications to chemical and metallurgical industries. The fee for a three years' course of study is eighty guineas, or per session of three months eight guineas.

Prospectuses, containing full particulars of the day and evening classes, may be had on application at the College.

DURHAM COLLEGE OF SCIENCE, NEWCASTLE-ON-TYNE.

Professor of Chemistry.—P. Phillips Bedson, M.A., D.Sc., F.I.C., F.C.S.

Lecturer in Chemistry.—Saville Shaw, F.C.S.

Lecturer in Agricultural Chemistry.—R. Greig Smith, B.Sc. (Edin.), F.C.S.

The Session will commence on September 23rd, 1895.

1. *General Course.*—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. A section of this Course will be devoted to an outline of Organic Chemistry. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 2nd. Fee, £3 10s. for the Session.

2. *Advanced Course.*—Inorganic Chemistry, Tuesdays 3 to 4 p.m., during the Session. Fee, £2; or for students taking Organic Chemistry, £1.

3. *Organic Chemistry.*—A Course of Lectures will be given throughout the Session, the subject of which will be Organic Chemistry, or the Chemistry of the Carbon Compounds. This class will meet on Tuesdays and Thursdays, at 11 a.m., and Fridays 3 to 4 p.m., and will commence on Thursday, October 3rd. Fee, £3 10s. for the Session.

Advanced Classes will be formed for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for the course, £3 10s.

A Lecture Course in Analytical Chemistry will be given on Mondays, at 3 p.m., commencing October 8th.

Metallurgy and Assaying.—Lecturer, Saville Shaw, F.C.S. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry-Assaying, and in the preparation and analysis of Alloys, &c. Fee as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of

special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10s.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees.*—Students working two days, £2 10s. per term, £6 per session; one day per week, £1 10s. per term, £3 10s. per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the title of Associate in Physical Science of the University of Durham. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must pass an examination on entrance, in reading, writing from dictation, English or Latin Grammar, arithmetic (including decimals), and geography. Registered students in medicine are exempted from this examination, or students who produce a certificate of having passed either of the two following examinations:—

1. Durham Examination for certificate of proficiency in General Education, held in March and September.
2. Durham Examination for Students in Arts in their first year, or any examination of a similar nature that may be accepted by the Council.

Associateship in Physical Science.—Every candidate for the Associateship in Physical Science will be required to satisfy the examiners in—Mathematics, Physics, Chemistry, and either Geology or Natural History—in an examination to be held at the end of the candidate's first year. Associates in Science are admissible one year after obtaining the title of Associate to examination for the degree of Bachelor of Science of the University of Durham.

Exhibitions.—Three Exhibitions of the value of £25, £15, and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Monday, September 23rd.

Evening Lectures.—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

Two Exhibitions of £15 each will be awarded at the next examination of "Persons not members of the University," which will be held at Durham in March next.

Several other valuable Scholarships are available for students.

OWENS COLLEGE, VICTORIA UNIVERSITY, MANCHESTER.

Professor and Director of the Chemical Laboratory.—Harold B. Dixon, M.A., F.R.S.

Professor of Organic Chemistry.—W. H. Perkin, Ph.D., F.R.S.

Demonstrators and Assistant Lecturers.—George H. Bailey, D.Sc., Ph.D.; Arthur Harden, M.Sc., Ph.D.; P. J. Hartog, B.Sc.; B. Lean, B.A., D.Sc.; and W. A. Bone, B.Sc., Ph.D.

Lecturer in Dyeing and Printing.—Ernest Bentz.

Assistant Lecturer in Metallurgy.—Gilbert J. Fowler, M.Sc.

The Session begins on October 1, 1895, and ends on June 23, 1896.

The instruction is given by means of Experimental Lectures and Tutorial Classes. The Chemical Classes form part of the Courses for Chemistry in the University.

Chemistry Lecture Courses.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

Introduction to Organic Chemistry.—Wednesdays and Fridays, at 9.30, during Lent Term.

These courses are intended for Medical Students and others beginning the study of chemistry.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30 a.m., during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Mondays, Wednesdays, Fridays, 3.30 p.m., during the two Winter Terms. The Metals.

Third Year Honours Course.—At times to be arranged. Physical Chemistry.

Organic Chemistry (General).—Tuesdays and Thursdays, 9.30, during two Winter Terms.

Organic Chemistry (Honours).—Mondays and Fridays, 9.30, during the two Winter Terms.

History of Chemistry and Chemical Philosophy.—Wednesdays, 10.30, during the Session.

METALLURGY.—*Lectures:* The Metallurgy of Copper, Lead, Silver, Gold, and the Metallurgy of Iron and Steel will be given in alternate years. *Practical:* Saturdays, 9.30.

The Chemical Laboratories are open daily from 9.30 a.m. to 4.30 p.m., except on Saturdays, when they are closed at 12.30 p.m.

Courses for B.Sc. Degree.—To qualify for the B.Sc. Degree of the Victoria University, Students have to attend a prescribed course of study extending over three years, and to pass the Preliminary Examination of the University either on entering or at the end of a year's Course.

The Honours Course of Chemistry is as follows:—*First year:* First year Honours Lectures; Mathematics (3 hours a week); Physics (3 hours a week); a Language (3 hours a week); Chemical Laboratory (3 days per week). *Second year:* Second year Honours Lectures; General Organic Lectures; Applied Chemistry Lectures; Physics Laboratory (1 day per week); Chemical Laboratory (3 days per week). *Third year:* Third year Honours Lectures; Honours Organic Lectures; History of Chemistry Lectures; Chemical Laboratory (5 days per week).

The following awards are made to successful Students in the Honours Examination:—A University Scholarship of £50; a Mercer Scholarship of £25. A University Fellowship of £150 is awarded annually among the Graduates in Science for the encouragement of Research. Among the College Scholarships open to Chemical Students are the Dalton Chemical Scholarship, £50 per annum for two years; the 1851 Exhibition Scholarship; the John Buckley Scholarship; &c.

Applied Chemistry.

First Course.—Sulphuric Acid and Alkali Manufactures. General Principles of Chemical Engineering.

Second Course.—The Chemistry of Fuel. The Manufacture of Illuminating Gas and Gaseous Fuel.

Third Course.—The Chemistry of Coal Tar.

Fourth Course.—Natural and Artificial Dye-stuffs.

Fifth Course.—Calico-printing.

Certificates in Applied Chemistry.

The course extends over a period of three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

Before admission to the first year's course students are required to give such evidence of elementary knowledge of Mathematics and Chemistry as shall be considered satisfactory by the Senate.

The first year's course is the same for all students working for the certificate.

In the second and third years a choice may be made between Inorganic and Organic Chemistry. By this division of the subject a student wishing to apply himself specially to the inorganic side of the science, may attend during his second year the Honours course in Metals, and courses on Geology or Mineralogy, and during his third year, courses on Metallurgy and on Geology or

Mineralogy; while a student wishing to apply himself specially to the organic side of the science, may attend during his second and third years the Courses on Organic Chemistry, and courses on the Coal Tar Colours and on Dyeing and Printing.

Part of the Laboratory practice in the second and third years will consist in the examination and analysis of raw materials, products from chemical works, &c., in connection with the special courses of lectures on Applied Chemistry. In the Chemistry and Physical laboratories the practical work in the second year will be arranged in accordance with the branch of Chemistry selected by the candidate.

In the third year the student, if sufficiently advanced, will be set to work on some analytical process or problem in Applied Chemistry, under the direction of the teaching staff.

UNIVERSITY COLLEGE, NOTTINGHAM.

DEPARTMENTS OF CHEMISTRY AND METALLURGY,
AND OF AGRICULTURE.

Professor of Chemistry.—Frank Clowes, D.Sc. Lond., F.I.C.

Demonstrators of Chemistry.—J. J. Sudborough, D.Sc., Ph.D., F.I.C., R. M. Caven, B.Sc., F.I.C., and G. Meland, B.Sc., A.R.S.M.

The Classes of the College are open to students of both sexes above sixteen years of age.

The dates of commencement and end of Terms in the Session 1895-96 will be as follows:—First Term, October 7th to December 21st; Second Term, January 20th to April 2nd; Third Term, April 20th to July 4th.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Non-Metals for the first two terms and for Elementary Organic Chemistry in the third term. In his second year he takes the course on Metals for the first two terms. In his third year he attends a course on Advanced Organic Chemistry or Applied Chemistry. Fee for Day Lectures and Classes: Non-Metals or Metals 42s.; Organic Chemistry (one term) 21s.; Advanced Organic Chemistry, 21s. per term.

Demonstrations and Lectures on Analytical Chemistry will be given in the day and evening, and should be attended by all students.

A Chemical Calculation Class is also held. Fee per Term, 5s.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry.—The chemical laboratory is open every day from 10 to 5, except on Saturday, when the hours are from 10 to 1, and on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to Pharmacy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees for day students: For one term, £7; for the session, £18; for six hours weekly 40s., and 5s. extra for each additional hour per week. For evening students, 10s. for two hours per week, three hours 15s., four hours 20s., six hours 30s., per term.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbering, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

Pharmaceutical Students can at all times work in the Chemical Laboratory, taking work suitable for the preparation for the Minor Examinations. Special lectures will also be given in Chemistry and *Materia Medica*.

Government Lectures and Classes.—Evening Lectures and Laboratory instruction will be given by the Demonstrators of Chemistry to Students who intend to present themselves for Examination by the Government Science and Art Department in May next. Inorganic, organic, and practical chemistry, agricultural chemistry, and metallurgy will be taught in the elementary, advanced, and honours stages, each of which commences at the beginning of the College Session in October. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

An Agricultural Course of instruction, extending over two years, is now organised under the general direction of Mr. M. J. R. Dunstan, M.A., F.R.S.E. It includes instruction in chemistry, botany, agriculture, with practical work on experimental fields, dairy work, farriery, land surveying, &c. The instruction is designed for those who intend to become farmers, bailiffs, land agents, or colonists, and may be extended to a third year if desired. Fee, £15 per annum for residents in Notts, £20 to residents in other counties.

Full information concerning all College Classes is given in the College Prospectus, price one penny.

FIRTH COLLEGE, SHEFFIELD.

Professor of Chemistry.—W. Carleton Williams, B.Sc., F.C.S.

Demonstrators and Assistant Lecturers.—G. Young, Ph.D., and L. T. O'Shea, B.Sc., F.C.S.,

The Session will commence on October 1st.

First Year's Course.—Chemistry of the Non-Metallic Elements. Tuesday and Friday from 10 to 11 a.m. Fee, £2 12s. 6d.

Second Year's Course.—Chemistry of Metals. Monday and Thursday from 10 to 11 a.m. £2 12s. 6d.

Third Year's Course.—Organic Chemistry, on Wednesday, from 9 to 10, and Saturday, from 10 to 11. Fee, £2 2s. Chemical Philosophy, Thursday, 11 to 12. Fee, £1 11s. 6d.

Short Courses of Lectures are also given by L. T. O'Shea on Electrolytic Analysis, and on the Chemistry of Coal Mining.

A Course of Lectures is arranged for Medical Students, with a special class in Qualitative Analysis.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Six hours per week, £5 5s.; Nine, £7; Twelve, £8 8s.; Eighteen, £11 5s.; Twenty-four, £14; Thirty-two, £17.

Day Students may not enter for less than six hours a week. Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

Fees for short periods (working thirty-two hours per week):—For one month, £3 3s.; two months, £5 5s.

An arrangement has been entered into with the Science and Art Department, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Department being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar.

Students who have worked for three sessions in the Chemical Laboratory are eligible for election to a scholarship value £150 for two years.

Evening Classes.—Lectures, Wednesday, 8 to 9. Laboratory instruction, Wednesday, 6 to 9, and another series to be arranged if desired. Sessional Fee, one evening per week, £1 10s.; two, 50s.; or Lecture Class and Laboratory, on Wednesday evening, £1 10s.

UNIVERSITY COLLEGE, DUNDEE.

Professor of Chemistry.—James Walker, Ph.D., D.Sc.
Assistant Lecturers.—F. J. Hambly, F.I.C., and J. R. Appleyard, F.C.S.

Lecture Assistant and Laboratory Steward.—J. Foggie, F.C.S.

The Winter Session begins on October 15th, and ends on March 21st. The Summer Session extends from May to July.

The First Year's Lecture Course on Systematic Chemistry is given daily during the Winter Session, and embraces the Elements of Inorganic and of Organic Chemistry.

Advanced Courses, of about fifty lectures each, will be given during the year as follows:—

Organic Chemistry; Inorganic Chemistry, including the more important technological applications; Theoretical and Physical Chemistry; Bleaching and Dyeing, including the Chemistry of the Textile Fibres.

Practical Instruction in all of the above branches will be given in the Laboratories and Dye-house. To supplement the Practical work of First Year's Laboratory Students a short course of Lectures on *Analytical Chemistry* will be offered. Special facilities are afforded to Research Students.

The Lectures and Laboratory Practice in Chemistry are recognised by the Medical Colleges of London and Edinburgh, as well as by the University of Edinburgh, for degrees in Science and Medicine. The Courses are suitable for the degrees of the University of London and for the Civil Service appointments, and will also satisfy the requirements of Students in Pharmacy, and of Students who intend to become candidates for the Associateship of the Institute of Chemistry, as far as qualification in Chemistry is concerned.

UNIVERSITY OF EDINBURGH.

DEPARTMENT OF CHEMISTRY.

Professor.—Alex. Crum Brown, M.D., D.Sc., F.R.S., Pres. C.S.

Lecturers.—L. Dobbin, Ph.D., and H. Marshall, D.Sc.
Assistants.—W. W. Taylor, M.A., and A. F. Watson, B.Sc.

The working terms are—Winter Session, from middle of October to middle of March; Summer Session, from beginning of May to end of July.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical and science students is given by the Professor. The class meets daily; fee £4 4s. An Advanced Course of twenty-five lectures is also given in the Winter Session; fee, £2 2s. A class on Organic Chemistry is held in summer; fee, £2 2s. There is also a class on Chemical Theory, by Dr. Dobbin; fee £1 1s.: and a class on Crystallography, by Dr. Marshall; fee, £2 2s.

In addition to the above, Lecture Courses are given by the Assistants on some particular branch of Organic and Inorganic Chemistry. These Lectures are free to Laboratory Students.

Tutorial classes are held in connection with the General Course.

Laboratories.—Practical classes for Medical Students meet daily during the latter part of the Winter Session and in the Summer Session. (Fee, £3 3s.) The laboratories for analytical and advanced practical work are open daily from 10 till 4. (Fees: Whole Day—Winter Session, £10 10s., Oct.-Dec., Jan.-March; or Summer Session, £5 5s. Half Day—Winter Session, £6 6s., Oct.-Dec., Jan.-March; or Summer Session, £3 3s. Preference will be given to students in the above order. Students who are not Matriculated may attend the Chemical Laboratory on payment of the entrance fee of 5s. in addition to the Laboratory fees. Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry. Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical languages, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy, and Chemistry. The Second B.Sc. Examination includes any three or more of the following subjects:—1. Mathematics. 2. Natural Philosophy. 3. Astronomy. 4. Chemistry. 5. Human Anatomy, including Anthropology. 6. Physiology. 7. Geology, including Mineralogy. 8. Zoology, including Comparative Anatomy. 9. Botany, including Vegetable Physiology. Chemistry in this examination includes Inorganic Chemistry, Organic Chemistry, Relation between Chemical and Physical Properties, Complex Qualitative Analysis (practical), Simple Quantitative Determinations (practical), and Gas Analysis (practical).

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry may be required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Professor.—John Gibson, Ph.D., F.R.S.E.

Assistant Professor.—John E. Mackenzie, Ph.D., B.Sc.

Demonstrators.—Andrew F. King and James B. Shand.

The Session begins October 8th, 1895.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

The Lecture Course to day students in Chemistry is mainly devoted to Inorganic Chemistry. In the Laboratory course each student is required to prepare and study the properties of the principal elementary and compound gases; to perform the more important experiments shown by the Professor in the Lecture Room; to make himself thoroughly acquainted with the preparation and purification of a number of salts. After a careful study of the reactions of the principal metals and acids, he passes on to a full course of systematic qualitative analysis, and may then, if attending a second year, take up an extensive course of quantitative analysis (gravimetric, volumetric, and electrolytic), ultimately making a speciality of any branch of the subject which may be most necessary for his future work. Great attention has been paid to the thorough equipment of the Advanced Laboratories, and special facilities are given to advanced students who may wish to engage in any class of Research (Inorganic or Organic) whether of a purely chemical or of a technical nature.

The teaching in the Evening Classes is based on the Syllabus of the Science and Art Department, and includes Elementary, Advanced, and Honours Courses in Theoretical and Practical Inorganic and Organic Chemistry.

GLASGOW AND WEST OF SCOTLAND

TECHNICAL COLLEGE.

Professor of Chemistry.—G. G. Henderson, D.Sc., M.A.

Professor of Technical Chemistry.—E. J. Mills, D.Sc., F.R.S.

Assistants.—J. Hendrick, B.Sc., F.I.C., A. R. Ewing, Ph.D., and T. Gray, B.Sc., F.C.S.

Professor of Metallurgy.—A. Humboldt Sexton, F.C.S., F.R.S.E.

The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following an industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College' the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan's Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments.

Complete courses of instruction in Metallurgy and Mining will be given in both Day and Evening Classes.

Copies of the Calendar for 1895-96 may be had from Mr. John Young, B.Sc., the Secretary, 38, Bath Street, Glasgow, price by post, 1s. 4d.

UNIVERSITY OF ST. ANDREWS.

UNITED COLLEGE OF ST. LEONARD AND ST. SALVATOR.

Professor of Chemistry.—T. Purdie, B.Sc., Ph.D., F.R.S.

The Session begins on October 10th. A Competitive Examination, open to intending Students of Arts or Science, for about forty-five Entrance Bursaries, ranging in value from £40 to £110 each per annum, will be held in the beginning of October. About thirty of these Bursaries, are restricted to Men and thirteen to Women, seven of the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine. Two are open to students of either sex. Two Scholarships of £100 each, tenable for one year, will be open for competition to Graduates of Science at the close of Session 1895-96. A Hall of Residence is provided for Women Students. Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree; the regulations will be found in the "University Calendar."

Lecture Courses.

Two distinct Courses of Lectures are given, each comprising at least one hundred meetings of the class.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically. Elementary Organic Chemistry is also included in the Course.

The chemistry of manufactures is referred to only cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment. The Lectures are supplemented by a short Course

of Laboratory Practice, intended to illustrate the principles of the science.

These courses of instruction are intended to meet the requirements of the Arts' Curriculum; also of candidates for the First B.Sc. Examination, and of students of medicine, so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part treats of the General Principles and Theory of Chemistry, and of more advanced Inorganic Chemistry, the instruction in general being such as is required for the Second B.Sc. Examination.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £10 is awarded to the best Student of the year.

Fee for the Session, for each Course, £3 3s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis; (3) Original Investigation. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the First and Second B.Sc. Examinations, and for Students of Medicine.

The fees for Practical Chemistry vary according to the number of hours taken weekly. A certain number of working places in the Laboratory will be available without fee for students who are capable of undertaking original investigation.

QUEEN'S COLLEGE, BELFAST.

Professor.—E. A. Letts, Ph.D., D.Sc., F.R.S.E., &c.

I.—Chemistry.—The lectures are delivered at 3 p.m., on the first five days of each week until the beginning of April, and on three days of each week after May 1st, at 2 p.m. The course is divided into three parts:—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry.

II.—Advanced and Organic Chemistry.—Lectures on these subjects are given during the first or second terms, or from May 1st until the middle of July, as may suit the convenience of the class. Fee, £1.

III.—Practical Chemistry.—In this course the Students are instructed in the general methods of conducting Chemical Analyses. Fee, £3.

IV.—Laboratory Pupils.—The Chemical Laboratories is open from November until the end of March, and from May 1st until the third week of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

Scholarships.—In addition to various Scholarships awarded in the Faculties of Arts and Medicine in which Chemistry forms a part of the examination, there are other valuable Scholarships awarded specially in connection with the schools of Chemistry and Physics.

QUEEN'S COLLEGE, CORK.

Professor.—Augustus E. Dixon, M.D.

Assistant.—D. J. O'Mahony, F.C.S.

The College Session begins on October 17th, 1895, and ends on June 8th, 1896. The classes are open to male and female students.

Systematic Chemistry.—(1) General course of Inorganic Chemistry, Elementary Organic Chemistry, and Chemical Philosophy.—Fee for each Sessional Course, £2. Each subsequent Course, £1. (2) Advanced Organic Chemistry, and Chemical Philosophy.

Practical Chemistry.—(1) The General Course of Practical Chemistry, consisting of about forty Lectures of two hours each, begins on January 7th, 1895.—Fee for each Sessional Course, £3. (2) A Course for Pharmaceutical Students. (3) Special Courses.

The Chemical Laboratory is open daily from 10 to 4 o'clock (except during class hours and on Saturdays) under the Superintendence of the Professor, to Students entering for special courses of qualitative and quantitative analysis; organic chemistry; or for the purpose of original investigation.

QUEEN'S COLLEGE, GALWAY.

Professor.—Alfred Senior, Ph.D., M.D., F.I.C.

Demonstrator.—A. J. Walker.

The College Session is divided into three terms. The First Term extends from October 15 to December 21, the Second Term from January 6 to March 28, and the Third Term from April 13 to June 13.

Chemistry is studied by attendance at Lectures, by work in the Laboratories, and by the use of the College Library. The Courses in the several faculties are arranged with a view to the requirements of the Royal University of Ireland, but are adapted also to those of other Universities and licensing bodies.

Lecture Courses.—1. First year's Course, Arts and Engineering, embraces Inorganic and the Elements of General Chemistry. 2. First year's Course, Medicine, includes Inorganic and Elementary Organic Chemistry. 3. Third year's Course, Arts, is devoted to Advanced Organic Chemistry.

Laboratory Courses.—1. Second year's Course, Arts and Engineering, consists of Exercises in Inorganic Qualitative Analysis. 2. Second year's Course, Medicine, includes Inorganic and Elementary Organic Qualitative Analysis and the Chemical Examination of Urine. 3. Third year's Course, Arts, embraces Quantitative Analysis and other experiments to suit the requirements of individual Students. 4. The Laboratories are also open to Students for work in other branches of Chemistry.

For Fees and other particulars apply to the Registrar, from whom the Calendar, published in December, and the Extracts from Calendar, published in advance in July, may be obtained.

ROYAL COLLEGE OF SCIENCE FOR IRELAND, STEPHEN'S GREEN, DUBLIN.

(SCIENCE AND ART DEPARTMENT).

Professor of Chemistry.—W. N. Hartley, F.R.S.

Assistant Chemist.—Hugh Ramage, F.I.C., Associate of the Royal College of Science, Dublin.

Demonstrator of Chemistry and Assaying.—(Vacant).

The Session commences on Monday, October 1st, 1894, and ends on June 21st, 1895.

The Royal College of Science for Ireland supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Mining, Engineering, and Manufactures. The Diploma of Associate of the Royal College of Science in the Faculty of Manufactures is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Chemistry; (2) Advanced Chemistry, including Chemical Manufactures and Metallurgy; (3) Analytical and Experimental Chemistry; (4) Instructions in Chemical Research.

Fees payable by Associate Students in the Faculty of Manufactures:—For the entire Course—first year, £10; second year, £25; third year, £12.

Fees payable by Non-Associates:—£2 for each separate

Course of Lectures. For Analytical Chemistry and Research—£2 for a special course of one month; £5 for three months; £9 for six months; £12 for the entire session. For Assaying—£5 for three months; £9 for six months; £12 for the entire session.

NOTE.—Important changes have been made in the Curriculum by which the First Year's Course of study has been simplified. Full particulars are contained in the Directory of the College, which may be had on application to the Secretary.

The following are supplementary courses of instruction arranged for those who are attending a Course of Lectures:—

- (1) Laboratory Instruction in the Theory of Chemistry.
- (2) An Analytical Course for Students in Engineering.
- (3) A Course of Practical Chemistry for Medical Students.
- (4) The Analysis of Water, Air, Food, and Drugs, intended for the instruction of Public Analysts and Medical Officers of Health.
- (5) Assaying.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College. There are also nine Royal Exhibitions attached to the College, of the yearly value of £50 each, with Free Education, including Laboratory Instruction, tenable for three years; three become vacant each year, and are competed for at the May Examinations of the Department of Science and Art.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

CITY AND GUILDS OF LONDON INSTITUTE FOR THE ADVANCEMENT OF TECHNICAL EDUCATION.—The operations of the City and Guilds of London Institute are divided broadly into four branches: the educational work of three London Colleges, and of the Technological Examinations. Programmes of the London Colleges may be had on application to the Head Office of the Institute, Gresham College, Basinghall Street, London, E.C., or from the respective Colleges. The Technological Examinations (Examinations Department, Exhibition Road, S.W.), are conducted once every year at various centres throughout the kingdom. Programme, with Syllabus of Subjects, &c., may be obtained of Messrs. Whittaker and Co., Paternoster Square, London, or through any bookseller, price 10d., net.—*City and Guilds Technical College, Exhibition Road.*—Professor of Chemistry, H. E. Armstrong, Ph.D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of industry, whether Manufactures or Arts. The main purpose of the instruction given is to point out the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons who are training to become Technical Teachers; 2. Persons who are preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. The Matriculation Examinations will begin on Tuesday, Sept. 17th, and

the Winter Session opens on Tuesday, October 1st. *City and Guilds Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in special subjects. An examination for the admission of Students will be held at the College at 10 o'clock on Tuesday, September 17th, 1895. *South London Technical Art School.*—Classes in Modelling, Design, Wood Engraving, Drawing and Painting, House Decoration, Machine Drawing and Design, Plaster-work, &c.

ADDEY'S SCIENCE AND ART SCHOOL, Church Street, Deptford.—Head Master, William Ping, F.C.S.—Day and Evening Classes in Theoretical and Practical Chemistry, Physics, &c. The Classes are approved by the County Council.

BIRKBECK LITERARY AND SCIENTIFIC INSTITUTION: BREAM'S BUILDINGS, CHANCERY LANE.—*Chemistry*, Courses will be conducted, commencing September 24th, adapted for the Elementary, Advanced, and Honours Examinations of the Science and Art Department, and for the Matriculation, B.Sc., and M.B. Degrees of the London University. *Inorganic Chemistry*: Mr. J. Woodward, B.A., B.Sc. Lectures—Elementary, Tuesdays, 8.15 p.m.; Advanced, Thursdays, 6.15; Practical, Tuesdays, 6—8 p.m.; Thursdays, 7.30—9.30 p.m. *Organic Chemistry*: Mr. F. Gossling, B.Sc. Lectures—Elementary, Wednesdays, 6 to 7 p.m.; Practical, Wednesdays, 7 to 9 p.m.

THE CENTRAL SCHOOL OF CHEMISTRY AND PHARMACY, 173, Marylebone Road, London.—Dr. A. B. Griffiths, F.R.S.E., F.C.S., &c., and Mr. Lionel Cooper, F.C.S. Lectures are given on Chemistry, Physics, Botany, Materia Medica, Pharmacy, &c. Laboratory Instruction.

SOUTH LONDON SCHOOL OF PHARMACY, Lim., 325, Kennington Road, S.E.—Lectures on Chemistry and Physics, by Dr. John Muter, F.R.S.E., F.I.C., Daily, at 9 a.m. (Organic) and 10 a.m. (Inorganic). Lectures on Botany daily at 12 noon, and at 2 p.m. on Materia Medica and Pharmacy, by Mr. Dodd, F.C.S. The Laboratories for Qualitative and Quantitative Analysis open daily from 9 till 5, under the direction of Mr. de Koningh, F.I.C., F.C.S. The Students' Laboratory of this Institution is specially designed to accommodate 40 Students. The Technical Laboratory is open daily from 9 till 5, and is fully fitted with all apparatus for teaching the manufacture of drugs and chemicals. Periodical Examinations of the Students are held by Visiting Examiners appointed by the Council of Education, and Medals and Certificates are awarded on the results thereof. Fees for the first three months 12 guineas; afterwards 24 guineas per month respectively, inclusive of all departments.

THE GOLDSMITHS' INSTITUTE, New Cross, S.E.—Head of the Chemistry Department, Mr. A. G. Bloxam, F.I.C.; Assistants, Mr. H. C. L. Bloxam and Mr. Percy Tarver, A.R.C.S. Lectures and Practical Classes in General Chemistry, also in Chemistry applied to Leather Manufacture and Gas Manufacture, are held in the evenings from 7.30 to 10.0, and are open to both sexes.

PEOPLE'S PALACE, Mile End Road, E. (Draper's Company's Institute).—Professor, J. T. Hewitt, M.A., D.Sc., Ph.D.; Assistant, Mr. F. G. Pope. The classes are open to both sexes without limit of age. Evening classes in Theoretical and Practical Chemistry. The Session commences on Monday, September 23rd. A course for the London University B.Sc. Degree, including Honours,

is now offered, and the Chemical Laboratory has been newly equipped. Every facility is offered to Students desiring to undertake Research work.

POLYTECHNIC INSTITUTE, 309, Regent Street, London, W.—Mr. R. A. Ward and Assistants.—Evening Classes in Theoretical and Practical Chemistry, &c.. The Classes are open to both sexes. The next term commences on October 1st, 1894.

UNIVERSITY TUTORIAL COLLEGE, 32, Red Lion Square, Holborn, W.C. (Science Department of the Univ. Coll.).—The large Chemical, Biological, and Physical laboratories have been found admirably suited to their purpose, and the proportion of passes in the London University Science Lists has increased rapidly. Students may work either for long or short periods.

WESTMINSTER COLLEGE OF CHEMISTRY AND PHARMACY, Trinity Square, Borough, S.E.—Messrs. Wills and Wootton. Day and Evening Classes.

BRISTOL MEDICAL SCHOOL.—Mr. T. Coomber, F.C.S.

THE CLIFTON LABORATORY, Berkeley Square, Bristol.—Students are received either as Private Pupils or Members of a Class. Instruction is given to those requiring to use science or scientific methods in Commercial and Industrial pursuits, or in preparing for Examinations. Every effort is made to produce thorough chemists rather than successful examinees.

LEEDS SCHOOL OF SCIENCE AND TECHNOLOGY, (Mechanics' Institution, Leeds).—There is a three years' course of lectures in Inorganic Chemistry, and a two years' course in Organic Chemistry and Metallurgy.

INSTITUTE OF CHEMICAL TECHNOLOGY, Hackins Hey, Liverpool (A. Norman Tate and Co.).—Principal, Mr. F. H. Tate, F.C.S. The course of instruction is intended more especially for students who wish to gain a knowledge of chemistry and the allied sciences in their relation to industrial and commercial pursuits, and embraces a thorough preliminary course of theoretical chemistry and practical laboratory work, followed by instruction in chemical technology fitted to the requirements of each pupil. In addition to these chemical studies, students who desire it can enter upon a special course calculated to afford them knowledge useful in the erection and arrangement of manufactories and plant, and construction of apparatus.

THE MUNICIPAL TECHNICAL SCHOOL, Princess Street, Manchester.—Theoretical and Practical Chemistry, Mr. E. Knecht, Ph.D., F.I.C., and Mr. J. Grant, F.I.C., F.C.S. Metallurgy, Mr. E. L. Rhead. At this important Municipal School, with an attendance of upwards of 3000 Students, there are organised Day Courses in Pure Chemistry, with applications to Dyeing, Bleaching, and Printing. In addition there are Evening Courses, not only in Pure Chemistry, but in Metallurgy, Iron and Steel Manufacture, Brewing, Oils, Colours and Varnishes, Oils and Fats, Soap Manufacture, Bleaching, Dyeing, and Printing, Coal Tar Products, Paper Manufacture, and Photography. The complete Syllabus (4d., by post 6d.) may be obtained on application to Mr. J. H. Reynolds, Director and Secretary, Princess Street, Manchester.

HIGHER GRADE SCHOOL, PATRICROFT.—Science and Art Day and Evening School, and Institute for Women. Demonstrator in Chemistry, Mr. R. J. B. Sanderson.

TECHNICAL INSTITUTE, Birley Street, Beswick.—Demonstrator in Chemistry, Mr. R. J. B. Sanderson.

SHEFFIELD BOROUGH ANALYSTS' LABORATORY, 1, Surrey Street.—Mr. A. H. Allen, F.C.S. Day and Evening Classes.

STOCKPORT TECHNICAL SCHOOL.—Department of Chemistry and Dyeing.—Principal: Mr. R. J. Brown, M.Sc. A syllabus with full particulars of the courses of instruction, hours, fees, &c., is obtainable on application.

TECHNICAL INSTITUTE, SWANSEA.—Classes in Theoretical and Practical Organic and Inorganic Chemistry, Metallurgy, Hygiene, Mathematics, &c., from October to May. Principal, W. Morgan, Ph.D., F.I.C.

ABERDEEN UNIVERSITY.—Prof. Japp.

SCHOOL OF MEDICINE, Edinburgh.—Dr. S. Macadam, Mr. King, Mr. I. Macadam, Mr. Paterson, and Drs. Aitken and Readman.

SURGEON'S HALL, Nicolson Street, Edinburgh.—Mr. Ivion Macadam. Laboratory work and demonstrations in Agricultural Chemistry. Chemistry Class for Women.

ST. MUNGO'S COLLEGE AND SCHOOL OF MEDICINE, EDINBURGH.—Dr. Marshall.

CITY ANALYST'S LABORATORY AND CLASS ROOM, 138, Bath Street, Glasgow.—Messrs. Wallace and Clark.

GLASGOW UNIVERSITY.—Prof. J. Ferguson.

GLASGOW VETERINARY COLLEGE.—Professor Cooke.

ANDERSON'S COLLEGE, GLASGOW.—Mr. J. R. Watson.

ROYAL COLLEGE OF SURGEONS IN IRELAND, DUBLIN.—Professor of Chemistry and Hygiene: Sir Charles A. Cameron, M.D., F.R.C.S.I. Instruction is given in the College Laboratory in General, Practical, and Analytical Chemistry, and in the subjects (Physical, Chemical, and Microscopical) required for Examinations in Public Health and to educate for the position of Public Analyst.

DUBLIN, CATHOLIC UNIVERSITY.—Dr. Campbell.

CORRESPONDENCE.

NEW GROUPING OF THE ELEMENTS.

To the Editor of the Chemical News.

SIR,—I suppose some of your readers, before this letter can reach you, will have drawn your attention to the fact that the "New Grouping of the Elements," given by Thomsen in the current volume of *Zeitsch. f. Anorganische Chemie*, pp. 190–193, is identical with the one given by Carnelley (*CHEMICAL NEWS*, vol. liii.), and by him accredited to Bayley (*Phil. Mag.*, 5, xiii., p. 26). These latter authors divide the third group of Thomsen.

It seems strange that Thomsen should have overlooked the previous publication of the table.—I am, &c.,

F. P. VENABLE.

Department of Chemistry,
University of North Carolina,
August 17, 1895.

The Drug, Chemical, and Allied Trades Exhibition.—This useful Trade Exhibition will be opened at the Agricultural Hall, Islington, N., on Tuesday next, September 10th, and will be continued on the three following days. Exhibits have been received from most of the leading houses, and should form an interesting and varied display. The Manager will forward invitation tickets to any gentlemen connected with the trade who desire to attend. The Offices of the Exhibition are at 42, Bishopsgate Without, E.C.

The Manner of the Action of Dry Hydrochloric Acid upon Serpentine.—E. A. Schneider.—In this reaction there is a formation of water. A part of the water formed escapes with the hydrochloric acid; another portion is retained by the residual silicate. This residue, on treatment with dry hydrogen chloride, behaves like the original mol. of serpentine. Water is formed along with magnesium chloride. A part of the water formed is retained by the residual silicate, and there ensues an absorption of water. In the experiments of Clarke and Schneider the hydrogen chloride used was sufficiently dried to be regarded as "dry."—*Zeit. Anorg. Chem.*

THE CHEMICAL NEWS.

VOL. LXXII., No. 1868.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

IPSWICH, 1895.

INAUGURAL ADDRESS OF THE PRESIDENT, SIR DOUGLAS GALTON, K.C.B., D.C.L., F.R.S.

My first duty is to convey to you, Mr. Mayor, and to the inhabitants of Ipswich, the thanks of the British Association for your hospitable invitation to hold our sixty-fifth meeting in your ancient town, and thus to recall the agreeable memories of the similar favour which your predecessors conferred on the Association forty-four years ago.

In the next place I feel it my duty to say a few words on the great loss which science has recently sustained—the death of the Right Hon. Thomas Henry Huxley. It is unnecessary for me to enlarge, in the presence of so many to whom his personality was known, upon his charm in social and domestic life; but upon the debt which the Association owes to him for the assistance which he rendered in the promotion of science I cannot well be silent. Huxley was pre-eminently qualified to assist in sweeping away the obstruction by dogmatic authority, which in the early days of the Association fettered progress in certain branches of science. For, whilst he was an eminent leader in biological research, his intellectual power, his original and intrepid mind, his vigorous and masculine English, made him a writer who explained the deepest subject with transparent clearness. And as a speaker his lucid and forcible style was adorned with ample and effective illustration in the lecture-room; and his energy and wealth of argument in a more public arena largely helped to win the battle of evolution, and to secure for us the right to discuss questions of religion and science without fear and without favour.

It may, I think, interest you to learn that Huxley first made the acquaintance of Tyndall at the meeting of the Association held in this town in 1851.

About forty-six years ago I first began to attend the meetings of the British Association, and I was elected one of your general secretaries about twenty-five years ago.

It is not unfitting, therefore, that I should recall to your minds the conditions under which science was pursued at the formation of the Association, as well as the very remarkable position which the Association has occupied in relation to science in this country.

Between the end of the sixteenth century and the early part of the present century several societies had been created to develop various branches of science. Some of these societies were established in London, and others in important provincial centres.

In 1831, in the absence of railways, communication between different parts of the country was slow and difficult. Science was therefore localised; and in addition to the universities in England, Scotland, and Ireland, the towns of Birmingham, Manchester, Plymouth, and York each maintained an important nucleus of scientific research.

ORIGIN OF THE BRITISH ASSOCIATION.

Under these social conditions the British Association was founded in September, 1831.

The general idea of its formation was derived from a migratory society which had been previously formed in

Germany; but whilst the German society met for the special occasion on which it was summoned, and then dissolved, the basis of the British Association was continuity.

The objects of the founders of the British Association were enunciated in their earliest rules to be:—

“To give a stronger impulse and a more systematic direction to scientific inquiry; to promote the intercourse of those who cultivated science in different parts of the British Empire with one another, and with foreign philosophers; to obtain a more general attention to the objects of science, and a removal of any disadvantages of a public kind which impede its progress.”

Thus the British Association for the Advancement of Science based its utility upon the opportunity it afforded for combination.

The first meeting of the Association was held at York with 353 members.

As an evidence of the want which the Association supplied, it may be mentioned that at the second meeting, which was held at Oxford, the number of members was 435. The third meeting, at Cambridge, numbered over 900 members; and at the meeting in Edinburgh in 1834 there were present 1298 members.

At its third meeting, which was held at Cambridge in 1833, the Association, through the influence it had already acquired, induced the Government to grant a sum of £500 for the reduction of the astronomical observations of Baily. And at the same meeting the General Committee commenced to appropriate to scientific research the surplus from the subscriptions of its members. The committees on each branch of science were desired “to select definite and important objects of science, which they may think most fit to be advanced by an application of the funds of the society, either in compensation for labour or in defraying the expense of apparatus, or otherwise, stating their reasons for their selection, and, when they may think proper, designating individuals to undertake the desired investigations.”

The several proposals were submitted to the Committee of Recommendations, whose approval was necessary before they could be passed by the General Committee. The regulations then laid down still guide the Association in the distribution of its grants. At that early meeting the Association was enabled to apply £600 to these objects.

I have always wondered at the foresight of the framers of the constitution of the British Association, the most remarkable feature of which is the lightness of the tie which holds it together. It is not bound by any complex central organisation. It consists of a federation of Sections, whose youth and energy are yearly renewed by a succession of presidents and vice-presidents, whilst in each Section some continuity of action is secured by the less movable secretaries.

The governing body is the General Committee, the members of which are selected for their scientific work; but their controlling power is tempered by the law that all changes of rules, or of constitution, should be submitted to, and receive the approval of, the Committee of Recommendations. This committee may be described as an ideal Second Chamber. It consists of the most experienced members of the Association.

The administration of the Association in the interval between annual meetings is carried on by the Council, an executive body, whose duty it is to complete the work of the annual meeting (a) by the publication of its proceedings; (b) by giving effect to resolutions passed by the General Committee; (c) it also appoints the Local Committee and organises the *personnel* of each Section for the next meeting.

I believe that one of the secrets of the long-continued success and vitality of the British Association lies in this purely democratic constitution, combined with the compulsory careful consideration which must be given to suggested organic changes.

The Association is now in the sixty-fifth year of its existence. In its origin it invited the philosophical societies dispersed throughout Great Britain to unite in a co-operative union.

Within recent years it has endeavoured to consolidate that union.

At the present time almost all important local scientific societies scattered throughout the country, some sixty-six in number, are in correspondence with the Association. Their delegates hold annual conferences at our meetings. The Association has thus extended the sphere of its action: it places the members of the local societies engaged in scientific work in relation with each other, and brings them into co-operation with members of the Association and with others engaged in original investigations, and the papers which the individual societies publish annually are catalogued in our Report. Thus by degrees a national catalogue will be formed of the scientific work of these societies.

The Association has, moreover, shown that its scope is coterminous with the British Empire by holding one of its annual meetings at Montreal, and we are likely soon to hold a meeting in Toronto.

CONDITION OF CERTAIN SCIENCES AT THE FORMATION OF THE BRITISH ASSOCIATION.

The Association, at its first meeting, began its work by initiating a series of reports upon the then condition of the several sciences.

A rapid glance at some of these reports will not only show the enormous strides which have been made since 1831 in the investigation of facts to elucidate the laws of Nature, but it may afford a slight insight into the impediments offered to the progress of investigation by the mental condition of the community, which had been for so long satisfied to accept assumptions without undergoing the labour of testing their truth by ascertaining the real facts. This habit of mind may be illustrated by two instances selected from the early reports made to the Association. The first is afforded by the report made in 1832, by Mr. Lubbock, on "Tides."

This was a subject necessarily of importance to England as a dominant power at sea. But in England records of the tides had only recently been commenced at the dockyards of Woolwich, Sheerness, Portsmouth, and Plymouth, on the request of the Royal Society, and no information had been collected upon the tides on the coasts of Scotland and Ireland.

The British Association may feel pride in the fact that within three years of its inception, viz., by 1834, it had induced the Corporation of Liverpool to establish two tide gauges, and the Government to undertake tidal observations at 500 stations on the coasts of Britain.

Another cognate instance is exemplified by a paper read at the second meeting, in 1832, upon the State of Naval Architecture in Great Britain. The author contrasts the extreme perfection of the carpentry of the internal fittings of the vessels with the remarkable deficiency of mathematical theory in the adjustment of the external form of vessels, and suggests the benefit of the application of refined analysis to the various practical problems which ought to interest shipbuilders—problems of capacity, of displacement, of stowage, of velocity, of pitching and rolling, of masting, of the effects of sails, and of the resistance of fluids; and, moreover, suggests that large scale experiments should be made by Government, to afford the necessary data for calculation.

Indeed, when we consider how completely the whole habit of mind of the populations of the Western world has been changed, since the beginning of the century, from willing acceptance of authority as a rule of life to a universal spirit of inquiry and experimental investigation, is it not probable that this rapid change has arisen from society having been stirred to its foundations by the causes and consequences of the French Revolution?

One of the earliest practical results of this awakening

in France was the conviction that the basis of scientific research lay in the accuracy of the standards by which observations could be compared; and the following principles were laid down as a basis for their measurements of length, weight, and capacity: viz. (1) that the unit of linear measure applied to matter in its three forms of extension, viz., length, breadth, and thickness, should be the standard of measures of length, surface, and solidity; (2) that the cubic contents of the linear measure in decimetres of pure water at the temperature of its greatest density should furnish at once the standard weight and the measure of capacity.* The metric system did not come into full operation in France till 1840, and it is now adopted by all countries on the continent of Europe except Russia.

The standards of length which were accessible in Great Britain at the formation of the Association were the Parliamentary standard yard lodged in the Houses of Parliament (which was destroyed in 1834 in the fire which burned the Houses of Parliament); the Royal Astronomical Society's standard; and the 10-foot bar of the Ordnance Survey.

The first two were assumed to afford exact measurements at a given temperature. The Ordnance bar was formed of two bars on the principle of a compensating pendulum, and afforded measurements independent of temperature. Standard bars were also disseminated throughout the country, in possession of the corporations of various towns.

The British Association early recognised the importance of uniformity in the record of scientific facts, as well as the necessity for an easy method of comparing standards and for verifying differences between instruments and apparatus required by various observers pursuing similar lines of investigation. At its meeting at Edinburgh in 1834 it caused a comparison to be made between the standard bar at Aberdeen, constructed by Troughton, and the standard of the Royal Astronomical Society, and reported that the scale "was exceedingly well finished; it was about $\frac{1}{160}$ th of an inch shorter than the 5-feet of the Royal Astronomical Society's scale, but it was evident that a great number of minute, yet important, circumstances have hitherto been neglected in the formation of such scales, without an attention to which they cannot be expected to accord with that degree of accuracy which the present state of science demands." Subsequently, at the meeting at Newcastle in 1863, the Association appointed a committee to report on the best means of providing for a uniformity of weights and measures with reference to the interests of science. This committee recommended the metric decimal system—a recommendation which has been endorsed by a committee of the House of Commons in the last session of Parliament.

British instrument-makers had been long conspicuous for accuracy of workmanship. Indeed, in the eighteenth century practical astronomy had been mainly in the hands of British observers; for although the mathematicians of France and other countries on the continent of Europe were occupying the foremost place in mathematical investigation, means of astronomical observation had been furnished almost exclusively by English artisans.

The sectors, quadrants, and circles of Ramsden, Bird, and Cary were inimitable by Continental workmen.

Lord Kelvin said in his Presidential Address at Edinburgh, "Nearly all the grandest discoveries of science have been but the rewards of accurate measurement and patient, long-continued labour in the sifting of numerical results." The discovery of argon, for which Lord Rayleigh and Professor Ramsay have been awarded the Hodgkin prize by the Smithsonian Institution, affords a remarkable illustration of the truth of this remark. In-

* The litre is the volume of a kilogramme of pure water at its maximum density, and is slightly less than the litre was intended to be, viz., one cubic decimetre. The weight of a cubic decimetre of pure water is 1.00013 kilogramme.

deed, the provision of accurate standards not only of length, but of weight, capacity, temperature, force, and energy, are amongst the foundations of scientific investigation.

In 1842 the British Association obtained the opportunity of extending its usefulness in this direction.

In that year the Government gave up the Royal Observatory at Kew, and offered it to the Royal Society, who declined it. But the British Association accepted the charge. Their first object was to continue Sabine's valuable observations upon the vibrations of a pendulum in various gases, and to promote pendulum observations in various parts of the world. They subsequently extended it into an observatory for comparing and verifying the various instruments which recent discoveries in physical science had suggested for continuous meteorological and magnetic observations, for observations and experiments on atmospheric electricity, and for the study of solar physics.

This new departure afforded a means for ascertaining the advantages and disadvantages of the several varieties of scientific instruments; as well as for standardising and testing instruments, not only for instrument makers, but especially for observers by whom simultaneous observations were then being carried on in different parts of the world; and also for training observers proceeding abroad on scientific expeditions.

Its special object was to promote original research, and expenditure was not to be incurred on apparatus merely intended to exhibit the necessary consequences of known laws.

The rapid strides in electrical science had attracted attention to the measurement of electrical resistances, and in 1859 the British Association appointed a special committee to devise a standard. The standard of resistance proposed by that committee became the generally accepted standard, until the requirements of that advancing science led to the adoption of an international standard.

In 1866 the Meteorological Department of the Board of Trade entered into close relations with the Kew Observatory.

And in 1871 Mr. Gassiot transferred £10,000 upon trust to the Royal Society for the maintenance of the Kew Observatory, for the purpose of assisting in carrying on magnetical, meteorological, and other physical observations. The British Association thereupon, after having maintained this Observatory for nearly thirty years, at a total expenditure of about £12,000, handed the Observatory over to the Royal Society.

The "Transactions" of the British Association are a catalogue of its efforts in every branch of science, both to promote experimental research and to facilitate the application of the results to the practical uses of life.

But probably the marvellous development in science which has accompanied the life history of the Association will be best appreciated by a brief allusion to the condition of some of the branches of science in 1831 as compared with their present state.

GEOLOGICAL AND GEOGRAPHICAL SCIENCE.

Geology.

At the foundation of the Association geology was assuming a prominent position in science. The main features of English geology had been illustrated as far back as 1821, and, among the founders of the British Association, Murchison and Phillips, Buckland, Sedgwick, and Conybeare, Lyell and De la Beche, were occupied in investigating the data necessary for perfecting a geological chronology by the detailed observations of the various British deposits, and by their co-relation with the Continental strata. They were thus preparing the way for those large generalisations which have raised geology to the rank of an inductive science.

In 1831 the Ordnance maps published for the southern counties had enabled the Government to recognise the

importance of a geological survey by the appointment of Mr. De la Beche to affix geological colours to the maps of Devonshire and portions of Somerset, Dorset, and Cornwall; and in 1835 Lyell, Buckland, and Sedgwick induced the Government to establish the Geological Survey Department, not only for promoting geological science, but on account of its practical bearing on agriculture, mining, the making of roads, railways, and canals, and on other branches of national industry.

Geography.

The Ordnance Survey appears to have had its origin in a proposal of the French Government to make a joint measurement of an arc of the meridian. This proposal fell through at the outbreak of the Revolution; but the measurement of the base for that object was taken as a foundation for a national survey. In 1831, however, the Ordnance Survey had only published the 1-inch map for the southern portion of England, and the great triangulation of the kingdom was still incomplete.

In 1834 the British Association urged upon the Government that the advancement of various branches of science was greatly retarded by the want of an accurate map of the whole of the British Isles; and that, consequently, the engineer and the meteorologist, the agriculturist and the geologist, were each fettered in their scientific investigations by the absence of those accurate data which now lie ready to his hand for the measurement of length, of surface, and of altitude.

Yet the first decade of the British Association was coincident with a considerable development of geographical research. The Association was persistent in pressing on the Government the scientific importance of sending the expedition of Ross to the Antarctic and of Franklin to the Arctic regions. We may trust that we are approaching a solution of the geography of the North Pole; but the Antarctic regions still present a field for the researches of the meteorologist, the geologist, the biologist, and the magnetic observer, which the recent voyage of M. Borchgrevink leads us to hope may not long remain unexplored.

In the same decade the question of an alternative route to India by means of a communication between the Mediterranean and the Persian Gulf was also receiving attention, and in 1835 the Government employed Colonel Chesney to make a survey of the Euphrates valley in order to ascertain whether that river would enable a practicable route to be formed from Iskanderoon, or Tripoli, opposite Cyprus, to the Persian Gulf. His valuable surveys are not, however, on a sufficiently extensive scale to enable an opinion to be formed as to whether a navigable waterway through Asia Minor is physically practicable, or whether the cost of establishing it might not be prohibitive.

The advances of Russia in Central Asia have made it imperative to provide an easy, rapid, and alternative line of communication with our Eastern possessions, so as not to be dependent upon the Suez Canal in time of war. If a navigation cannot be established, a railway between the Mediterranean and the Persian Gulf has been shown by the recent investigations of Messrs. Hawkshaw and Hayter, following on those of others, to be perfectly practicable and easy of accomplishment; such an undertaking would not only be of strategical value, but it is believed it would be commercially remunerative.

Speke and Grant brought before the Association, at its meeting at Newcastle in 1863, their solution of the mystery of the Nile basin, which had puzzled geographers from the days of Herodotus; and the efforts of Livingstone and Stanley and others have opened out to us the interior of Africa. I cannot refrain here from expressing the deep regret which geologists and geographers, and indeed all who are interested in the progress of discovery, feel at the recent death of Joseph Thomson. His extensive, accurate, and trustworthy observations added much to our knowledge of Africa, and by his premature death we have lost one of its most competent explorers.

CHEMICAL, ASTRONOMICAL, AND PHYSICAL SCIENCE.

Chemistry.

The report made to the Association on the state of the chemical sciences in 1832, says that the efforts of investigators were then being directed to determining with accuracy the true nature of the substances which compose the various products of the organic and inorganic kingdoms, and the exact ratios by weight which the different constituents of these substances bear to each other.

But since that day the science of chemistry has far extended its boundaries. The barrier has vanished which was supposed to separate the products of living organisms from the substances of which minerals consist, or which could be formed in the laboratory. The number of distinct carbon compounds obtainable from organisms has greatly increased; but it is small when compared with the number of such compounds which have been artificially formed. The methods of analysis have been perfected. The physical, and especially the optical, properties of the various forms of matter have been closely studied, and many fruitful generalisations have been made. The form in which these generalisations would now be stated may probably change, some, perhaps, by the overthrow or disuse of an ingenious guess at Nature's workings, but more by that change which is the ordinary growth of science—namely, inclusion in some simpler and more general view.

In these advances the chemist has called the spectro-scope to his aid. Indeed, the existence of the British Association has been practically coterminous with the comparatively newly-developed science of spectrum analysis, for though Newton,* Wollaston, Fraunhofer, and Fox Talbot had worked at the subject long ago, it was not till Kirchhoff and Bunsen set a seal on the prior labours of Stokes, Angström, and Balfour Stewart that the spectra of terrestrial elements have been mapped out and grouped; that by its help new elements have been discovered, and that the idea has been suggested that the various orders of spectra of the same elements are due to the existence of the element in different molecular forms—allotropic or otherwise—at different temperatures.

But great as have been the advances of terrestrial chemistry through its assistance, the most stupendous advance which we owe to the spectro-scope lies in the celestial direction.

Astronomy.

In the earlier part of this century, whilst the sidereal universe was accessible to investigators, many problems outside the solar system seemed to be unapproachable.

At the third meeting of the Association, at Cambridge, in 1833, Dr. Whewell said that astronomy is not only the queen of science, but the only perfect science, which was "in so elevated a state of flourishing maturity that all that remained was to determine with the extreme of accuracy the consequences of its rules by the profoundest combinations of mathematics; the magnitude of its data by the minutest scrupulousness of observation."

But in the previous year, viz., 1832, Airy, in his report to the Association on the progress of astronomy, had pointed out that the observations of the planet Uranus could not be united in one elliptic orbit; a remark which turned the attention of Adams to the discovery of Neptune. In his report on the position of optical science in 1832, Brewster suggested that with the assistance of adequate instruments "it would be possible to study the action of the elements of material bodies upon rays of artificial light, and thereby to discover the analogies between their affinities and those which produce the fixed lines in

the spectra of the stars; and thus to study the effects of the combustions which light up the suns of other systems."

This idea has now been realised. All the stars which shine brightly enough to impress an image of the spectrum upon a photographic plate have been classified on a chemical basis. The close connection between stars and nebulae has been demonstrated; and while on the one hand the modern science of thermodynamics has shown that the hypothesis of Kant and Laplace on stellar formation is no longer tenable, inquiry has indicated that the true explanation of stellar evolution is to be found in the gradual condensation of meteoritic particles, thus justifying the suggestions put forward long ago by Lord Kelvin and Professor Tait.

We now know that the spectra of many of the terrestrial elements in the chromosphere of the sun differ from those familiar to us in our laboratories. We begin to glean the fact that the chromospheric spectra are similar to those indicated by the absorption going on in the hottest stars, and Lockyer has not hesitated to affirm that these facts would indicate that in those localities we are in the presence of the actions of temperatures sufficiently high to break up our chemical elements into finer forms. Other students of these phenomena may not agree in this view, and possibly the discrepancies may be due to default in our terrestrial chemistry. Still, I would recall to you that Dr. Carpenter, in his Presidential Address at Brighton in 1872, almost censured the speculations of Frankland and Lockyer in 1868 for attributing a certain bright line in the spectrum of solar prominences (which was not identifiable with that of any known terrestrial source of light) to a hypothetical new substance which they proposed to call "helium," because "it had not received that verification which, in the case of Crookes's search for thallium, was afforded by the actual discovery of the new metal." Ramsay has now shown that this gas is present in dense minerals on earth; but we have now also learned from Lockyer that it and other associated gases are not only found with hydrogen in the solar chromosphere, but that these gases, with hydrogen, form a large percentage of the atmospheric constituents of some of the hottest stars in the heavens.

The spectro-scope has also made us acquainted with the motions and even the velocities of those distant orbs which make up the sidereal universe. It has enabled us to determine that many stars, single to the eye, are really double, and many of the conditions of these strange systems have been revealed. The rate at which matter is moving in solar cyclones and winds is now familiar to us. And I may also add that quite recently this wonderful instrument has enabled Professor Keeler to verify Clerk-Maxwell's theory that the rings of Saturn consist of a marvellous company of separate moons—as it were, a cohort of courtiers revolving round their queen—with velocities proportioned to their distances from the planet.

Physics.

If we turn to the sciences which are included under physics, the progress has been equally marked.

In optical science, in 1831 the theory of emission as contrasted with the undulatory theory of light was still under discussion.

Young, who was the first to explain the phenomena due to the interference of the rays of light as a consequence of the theory of waves, and Fresnel, who showed the intensity of light for any relative position of the interference-waves, both had only recently passed away.

The investigations into the laws which regulate the conduction and radiation of heat, together with the doctrine of latent and of specific heat, and the relations of vapour to air, had all tended to the conception of a material heat, or caloric, communicated by an actual flow and emission.

It was not till 1834 that improved thermometrical appliances had enabled Forbes and Melloni to establish the polarisation of heat, and thus to lay the foundation of an

* Joannes Marcus Marci, of Kronland in Bohemia, was the only predecessor of Newton who had any knowledge of the formation of a spectrum by a prism. He not only observed that the coloured rays diverged as they left the prism, but that a coloured ray did not change in colour after transmission through a prism. His book, "Thaumantias, liber de arcu coelesti deque colorum apparentium natura," Prag, 1648, was, however, not known to Newton, and had no influence upon future discoveries.

undulatory theory for heat similar to that which was in progress of acceptance for light.

Whewell's report, in 1832, on magnetism and electricity shows that these branches of science were looked upon as cognate, and that the theory of two opposite electric fluids was generally accepted.

In magnetism, the investigations of Hansteen, Gauss, and Weber in Europe, and the observations made under the Imperial Academy of Russia over the vast extent of that empire, had established the existence of magnetic poles, and had shown that magnetic disturbances were simultaneous at all the stations of observation.

At their third meeting the Association urged the Government to establish magnetic and meteorological observatories in Great Britain and her colonies and dependencies in different parts of the earth, furnished with proper instruments, constructed on uniform principles, and with provisions for continued observations at those places.

In 1839 the British Association had a large share in inducing the Government to initiate the valuable series of experiments for determining the intensity, the declination, the dip, and the periodical variations of the magnetic needle, which were carried on for several years, at numerous selected stations over the surface of the globe, under the directions of Sabine and Lefroy.

In England systematic and regular observations are still made at Greenwich, Kew, and Stonyhurst. For some years past similar observations by both absolute and self-recording instruments have also been made at Falmouth—close to the home of Robert Were Fox, whose name is inseparably connected with the early history of terrestrial magnetism in this country—but under such great financial difficulties that the continuance of the work is seriously jeopardised. It is to be hoped that means may be forthcoming to carry it on. Cornishmen, indeed, could find no more fitting memorial of their distinguished countryman, John Couch Adams, than by suitably endowing the magnetic observatory in which he took so lively an interest.

Far more extended observation will be needed before we can hope to have an established theory as to the magnetism of the earth. We are without magnetic observations over a large part of the Southern Hemisphere. And Professor Rücker's recent investigations tell us that the earth seems as it were alive with magnetic forces, be they due to electric currents or to variations in the state of magnetised matter; that the disturbances affect not only the diurnal movement of the magnet, but that even the small part of the secular change which has been observed, and which has taken centuries to accomplish, is interfered with by some slower agency. And, what is more important, he tells us that none of these observations stand as yet upon a firm basis, because standard instruments have not been in accord; and much labour, beyond the power of individual effort, has hitherto been required to ascertain whether the relations between them are constant or variable.

In electricity, in 1831, just at the time when the British Association was founded, Faraday's splendid researches in electricity and magnetism at the Royal Institution had begun with his discovery of magneto-electric induction, his investigation of the laws of electro-chemical decomposition, and the mode of electrolytical action.

But, the practical application of our electrical knowledge was then limited to the use of lightning-conductors for buildings and ships. Indeed, it may be said that the applications of electricity to the use of man have grown up side by side with the British Association.

One of the first practical applications of Faraday's discoveries was in the deposition of metals and electroplating, which has developed into a large branch of national industry; and the dissociating effect of the electric arc, for the reduction of ores, and in other processes, is daily obtaining a wider extension.

But probably the application of electricity, which is

tending to produce the greatest change in our mental, and even material condition, is the electric telegraph and its sister, the telephone. By their agency not only do we learn, almost at the time of their occurrence, the events which are happening in distant parts of the world, but they are establishing a community of thought and feeling between all the nations of the world which is influencing their attitude towards each other, and, we may hope, may tend to weld them more and more into one family.

The electric telegraph was introduced experimentally in Germany in 1833, two years after the formation of the Association. It was made a commercial success by Cooke and Wheatstone in England, whose first attempts at telegraphy were made on the line from Euston to Camden Town in 1837, and on the line from Paddington to West Drayton in 1838.

The submarine telegraph to America, conceived in 1856, became a practical reality in 1861 through the commercial energy of Cyrus Field and Pender, aided by the mechanical skill of Latimer Clark, Gooch, and others, and the scientific genius of Lord Kelvin. The knowledge of electricity gained by means of its application to the telegraph, largely assisted the extension of its utility in other directions.

The electric light gives, in its incandescent form, a very perfect hygienic light. Where rivers are at hand the electrical transmission of power will drive railway trains and factories economically, and might enable each artisan to convert his room into a workshop, and thus assist in restoring to the labouring man some of the individuality which the factory has tended to destroy.

In 1843 Joule described his experiments for determining the mechanical equivalent of heat. But it was not until the meeting at Oxford, in 1847, that he fully developed the law of the conservation of energy, which, in conjunction with Newton's law of the conservation of momentum, and Dalton's law of the conservation of chemical elements, constitutes a complete mechanical foundation for physical science.

Who, at the foundation of the Association, would have believed some far-seeing philosopher if he had foretold that the spectroscopist would analyse the constituents of the sun and measure the motions of the stars; that we should liquefy air and utilise temperatures approaching to the absolute zero for experimental research; that, like the magician in the "Arabian Nights," we should annihilate distance by means of the electric telegraph and the telephone; that we should illuminate our largest buildings instantaneously, with the clearness of day, by means of the electric current; that by the electric transmission of power we should be able to utilise the Falls of Niagara to work factories at distant places; that we should extract metals from the crust of the earth by the same electrical agency to which, in some cases, their deposition has been attributed?

These discoveries and their applications have been brought to their present condition by the researches of a long line of scientific explorers, such as Dalton, Joule, Maxwell, Helmholtz, Hers, Kelvin, and Rayleigh, aided by vast strides made in mechanical skill. But what will our successors be discussing sixty years hence? How little do we yet know of the vibrations which communicate light and heat! Far as we have advanced in the application of electricity to the uses of life, we know but little even yet of its real nature. We are only on the threshold of the knowledge of molecular action, or of the constitution of the all-pervading æther. Newton, at the end of the seventeenth century, in his preface to the "Principia," says:—"I have deduced the motions of the planets by mathematical reasoning from forces; and I would that we could derive the other phenomena of Nature from mechanical principles by the same mode of reasoning. For many things move me, so that I somewhat suspect that all such may depend on certain forces by which the particles of bodies, through causes not yet known, are either urged towards each other according to regular

figures, or are repelled and recede from each other; and these forces being unknown, philosophers have hitherto made their attempts on Nature in vain."

In 1848 Faraday remarked:—"How rapidly the knowledge of molecular forces grows upon us, and how strikingly every investigation tends to develop more and more their importance."

"A few years ago magnetism was an occult force, affecting only a few bodies; now it is found to influence all bodies, and to possess the most intimate relation with electricity, heat, chemical action, light, crystallisation; and through it the forces concerned in cohesion. We may feel encouraged to continuous labours, hoping to bring it into a bond of union with gravity itself."

But it is only within the last few years that we have begun to realise that electricity is closely connected with the vibrations which cause heat and light, and which seem to pervade all space—vibrations which may be termed the voice of the Creator calling to each atom and to each cell of protoplasm to fall into its ordained position, each, as it were, a musical note in the harmonious symphony which we call the universe.

Meteorology.

At the first meeting, in 1831, Prof. James D. Forbes was requested to draw up a report on the State of Meteorological Science, on the ground that this science is more in want than any other of that systematic direction which it is one great object of the Association to give.

Professor Forbes made his first report in 1832, and a subsequent report in 1840. The systematic records now kept, in various parts of the world, of barometric pressure, of solar heat, of the temperature and physical conditions of the atmosphere at various altitudes, of the heat of the ground at various depths, of the rainfall, of the prevalence of winds, and the gradual elucidation not only of the laws which regulate the movements of cyclones and storms, but of the influences which are exercised by the sun and by electricity and magnetism, not only upon atmospheric conditions, but upon health and vitality, are gradually approximating meteorology to the position of an exact science.

England took the lead in rainfall observations. Mr. J. G. Symons organised the British Rainfall System in 1860 with 178 observers, a system which until 1876 received the help of the British Association. Now Mr. Symons himself conducts it, assisted by more than 3000 observers, and these volunteers not only make the observations, but defray the expense of their reduction and publication. In foreign countries this work is done by Government officers at the public cost.

At the present time a very large number of rain-gauges are in daily use throughout the world. The British Islands have more than 3000, and India and the United States have nearly as many; France and Germany are not far behind; Australia probably has more—indeed, one colony alone, New South Wales, has more than 1100.

The storm warnings now issued under the excellent systematic organisation of the Meteorological Committee may be said to have had their origin in the terrible storm which broke over the Black Sea during the Crimean War, on November 27th, 1855. Leverrier traced the progress of that storm, and, seeing how its path could have been reported in advance by the electric telegraph, he proposed to establish observing stations which should report to the coasts the probability of the occurrence of a storm. Leverrier communicated with Airy, and the Government authorised Admiral FitzRoy to make tentative arrangements in this country. The idea was also adopted on the Continent, and now there are few civilised countries north or south of the Equator without a system of storm warning.*

* It has often been supposed that Leverrier was also the first to issue a daily weather map, but that was not the case, for in the Great Exhibition of 1851 the Electric Telegraph Company sold daily

BIOLOGICAL SCIENCE.

Botany.

The earliest Reports of the Association which bear on the biological sciences were those relating to botany.

In 1831 the controversy was yet unsettled between the advantages of the Linnean, or Artificial system, as contrasted with the Natural system of classification. Histology, morphology, and physiological botany, even if born, were in their early infancy.

Our records show that von Mohl noted cell division in 1835, the presence of chlorophyll corpuscles in 1837; and he first described protoplasm in 1846.

Vast as have been the advances of physiological botany since that time, much of its fundamental principles remain to be worked out, and I trust that the establishment, for the first time, of a permanent Section for botany at the present meeting will lead the Association to take a more prominent part than it has hitherto done in the further development of this branch of biological science.

Animal Physiology.

In 1831 Cuvier, who during the previous generation had, by the collation of facts followed by careful inductive reasoning, established the plan on which each animal is constructed, was approaching the termination of his long and useful life. He died in 1832; but in 1831 Richard Owen was just commencing his anatomical investigations and his brilliant contributions to palæontology.

The impulse which their labours gave to biological science was reflected in numerous reports and communications, by Owen and others, throughout the early decades of the British Association, until Darwin propounded a theory of evolution which commanded the general assent of the scientific world. For this theory was not absolutely new. But just as Cuvier had shown that each bone in the fabric of an animal affords a clue to the shape and structure of the animal, so Darwin brought harmony into scattered facts, and led us to perceive that the moulding hand of the Creator may have evolved the complicated structures of the organic world from one or more primeval cells.

Richard Owen did not accept Darwin's theory of evolution, and a large section of the public contested it. I well remember the storm it produced—a storm of praise by my geological colleagues, who accepted the result of investigated facts; a storm of indignation, such as that which would have burned Galileo at the stake, from those who were not yet prepared to question the old authorities; but they diminish daily.

We are, however, as yet only on the threshold of the doctrine of evolution. Does not each fresh investigation, even into the embryonic stage of the simpler forms of life, suggest fresh problems?

Anthropology.

The impulse given by Darwin has been fruitful in leading others to consider whether the same principle of evolution may not have governed the moral as well as the material progress of the human race. . . . Evolution, as Sir William Flower said, is the message which biology has sent to help us on with some of the problems of human life, and Francis Galton urges that man, the foremost outcome of the awful mystery of evolution, should realise that he has the power of shaping the course of future humanity by using his intelligence to discover and expedite the changes which are necessary to adapt circumstances to man, and man to circumstances.

In considering the evolution of the human race, the science of preventive medicine may afford us some indication of the direction in which to seek for social improvement. One of the earliest steps towards establishing that

weather maps, copies of which are still in existence, and the data for them were, it is believed, obtained by Mr. James Glaisher, F.R.S., at that time Superintendent of the Meteorological Department at Greenwich.

science upon a secure basis was taken in 1835 by the British Association, who urged upon the Government the necessity of establishing registers of mortality showing the cause of death "on one uniform plan in all parts of the King's dominions, as the only means by which general laws touching the influence of causes of disease and death could be satisfactorily deduced." The general registration of births and deaths was commenced in 1838. But a mere record of death and its proximate cause is insufficient. Preventive medicine requires a knowledge of the details of the previous conditions of life and of occupation. Moreover, death is not our only or most dangerous enemy, and the main object of preventive medicine is to ward off disease. Disease of body lowers our useful energy. Disease of body or of mind may stamp its curse on succeeding generations.

The anthropometric laboratory affords to the student of anthropology a means of analysing the causes of weakness, not only in bodily, but also in mental life.

Mental actions are indicated by movements and their results. Such signs are capable of record, and modern physiology has shown that bodily movements correspond to action in nerve-centres, as surely as the motions of the telegraph-indicator express the movements of the operator's hands in the distant office.

Thus there is a relation between a defective status in brain power and defects in the proportioning of the body. Defects in physiognomical details, too finely graded to be measured with instruments, may be appreciated with accuracy by the senses of the observer; and the records show that these defects are, in a large degree, associated with a brain status lower than the average in mental power.

A report presented by one of your committees gives the results of observations made on 100,000 school children examined individually in order to determine their mental and physical condition for the purpose of classification. This shows that about 16 per 1000 of the elementary school population appear to be so far defective in their bodily or brain condition as to need special training to enable them to undertake the duties of life, and to keep them from pauperism or crime.

Many of our feeble-minded children, and much disease and vice, are the outcome of inherited proclivities. Francis Galton has shown us that types of criminals which have been bred true to their kind are one of the saddest disfigurements of modern civilisation; and he says that few deserve better of their country than those who determine to lead celibate lives through a reasonable conviction that their issue would probably be less fitted than the generality to play their part as citizens.

These considerations point to the importance of preventing those suffering from transmissible disease, or the criminal, or the lunatic, from adding fresh sufferers to the teeming misery in our large towns. And in any case, knowing as we do the influence of environment on the development of individuals, they point to the necessity of removing those who are born with feeble minds, or under conditions of moral danger, from surrounding deteriorating influences.

These are problems which materially affect the progress of the human race, and we may feel sure that, as we gradually approach their solution, we shall more certainly realise that the theory of evolution, which the genius of Darwin impressed on this century, is but the first step on a biological ladder which may possibly eventually lead us to understand how in the drama of creation man has been evolved as the highest work of the Creator.

Bacteriology.

The sciences of medicine and surgery were largely represented in the earlier meetings of the Association, before the creation of the British Medical Association afforded a field for their more intimate discussion. The close connection between the different branches of science is causing a revival in our proceedings of discussions on

some of the highest medical problems, especially those relating to the spread of infectious and epidemic disease.

It is interesting to contrast the opinion prevalent at the foundation of the Association with the present position of the question.

A report to the Association in 1834, by Professor Henry, on contagion, says:—

"The notion that contagious emanations are at all connected with the diffusion of animalculæ through the atmosphere is at variance with all that is known of the diffusion of volatile contagion."

Whilst it had long been known that filthy conditions in air, earth, and water fostered fever, cholera, and many other forms of disease, and that the disease ceased to spread on the removal of these conditions, yet the reason for their propagation or diminution remained under a veil.

Leeuwenhoek in 1680 described the yeast-cells, but Schwann in 1837 first showed clearly that fermentation was due the activity of the yeast-cells; and, although vague ideas of fermentation had been current during the past century, he laid the foundation of our exact knowledge of the nature of the action of ferments, both organised and unorganised. It was not until 1860, after the prize of the Academy of Sciences had been awarded to Pasteur for his essay against the theory of spontaneous generation, that his investigations into the action of ferments* enabled him to show that the effects of the yeast-cell are indissolubly bound up with the activities of the cell as a living organism, and that certain diseases, at least, are due to the action of ferments in the living being. In 1865 he showed that the disease of silk worms, which was then undermining the silk industry in France, could be successfully combated. His further researches into anthrax, fowl cholera, swine fever, rabies, and other diseases proved the theory that those diseases are connected in some way with the introduction of a microbe into the body of an animal; that the virulence of the poison can be diminished by cultivating the microbes in an appropriate manner; and that when the virulence has been thus diminished their inoculation will afford a protection against the disease.

Meanwhile it had often been observed in hospital practice that a patient with a simple-fractured limb was easily cured, whilst a patient with a compound fracture often died from the wound. Lister was thence led, in 1865, to adopt his antiseptic treatment, by which the wound is protected from hostile microbes.

These investigations, followed by the discovery of the existence of a multitude of micro-organisms and the recognition of some of them—such as the bacillus of tubercle and the comma bacillus of cholera—as essential factors of disease; and by the elaboration by Koch and others of methods by which the several organisms might be isolated, cultivated, and their histories studied, have gradually built up the science of bacteriology. Amongst later developments are the discovery of various so-called anti-toxins, such as those of diphtheria and tetanus, and the utilisation of these for the cure of disease. Lister's treatment formed a landmark in the science of surgery, and enabled our surgeons to perform operations never before dreamed of; whilst later discoveries are tending to place the practice of medicine on a firm scientific basis. And the science of bacteriology is leading us to recur to stringent rules for the isolation of infectious disease, and to the disinfection (by superheated steam) of materials which have been in contact with the sufferer.

These microbes, whether friendly or hostile, are all capable of multiplying at an enormous rate under favour-

* In speaking of ferments one must bear in mind that there are two classes of ferments: one, living beings, such as yeast—"organised" ferments, as they are sometimes called—the other the products of living beings themselves, such as pepsin, &c.,—"unorganised" ferments. Pasteur worked with the former, very little with the latter.

able conditions. They are found in the air, in water, in the soil; but, fortunately, the presence of one species appears to be detrimental to other species, and sunshine, or even light from the sky, is prejudicial to most of them. Our bodies, when in health, appear to be furnished with special means of resisting attacks, and, so far as regards their influence in causing disease, the success of the attack of a pathogenic organism upon an individual depends, as a rule, in part at least, upon the power of resistance of the individual.

But notwithstanding our knowledge of the danger arising from a state of low health in individuals, and of the universal prevalence of these micro-organisms, how careless we are in guarding the health conditions of every-day life! We have ascertained that pathogenic organisms pervade the air. Why, therefore, do we allow our meat, our fish, our vegetables, our easily-contaminated milk, to be exposed to their inroads, often in the foulest localities? We have ascertained that they pervade the water we drink, yet we allow foul water from our dwellings, our pig-sties, our farmyards, to pass into ditches without previous clarification, whence it flows into our streams and pollutes our rivers. We know the conditions of occupation which foster ill-health. Why, whilst we remove outside sources of impure air, do we permit the occupation of foul and unhealthy dwellings?

The study of bacteriology has shown us that although some of these organisms may be the accompaniments of disease, yet we owe it to the operation of others that the refuse caused by the cessation of animal and vegetable life is re-converted into food for fresh generations of plants and animals.

These considerations have formed a point of meeting where the biologist, the chemist, the physician, and the statistician unite with the sanitary engineer in the application of the science of preventive medicine.

ENGINEERING.

Sewage Purification.

The early reports to the Association show that the laws of hydrostatics, hydrodynamics, and hydraulics, necessary to the supply and removal of water through pipes and conduits, had long been investigated by the mathematician. But the modern sanitary engineer has been driven by the needs of an increasing population to call in the chemist and the biologist to help him to provide pure water and pure air.

The purification and the utilisation of sewage occupied the attention of the British Association as early as 1864, and between 1869 and 1876 a committee of the Association made a series of valuable reports on the subject. The direct application of sewage to land, though effective as a means of purification, entailed difficulties in thickly settled districts, owing to the extent of land required.

It was not till the chemist called to his aid the biologist that a scientific system of sewage purification was evolved. The valuable experiments made in recent years by the State Board of Health in Massachusetts have more clearly explained to us how by this system we may utilise micro-organisms to convert organic impurity in sewage into food fitted for higher forms of life.

To effect this we require, in the first place, a filter about 5 feet thick of sand and gravel, or, indeed, of any material which affords numerous surfaces or open pores. Secondly, that after a volume of sewage has passed through the filter, an interval of time be allowed, in which the air necessary to support the life of the micro-organisms is enabled to enter the pores of the filter. Thus this system is dependent upon oxygen and time. Under such conditions the organisms necessary for purification are sure to establish themselves in the filter before it has been long in use. Temperature is a secondary consideration.

Imperfect purification can invariably be traced either to a lack of oxygen in the pores of the filter, or to the

sewage passing through so quickly that there is not sufficient time for the necessary processes to take place. And the power of any material to purify either sewage or water depends almost entirely upon its ability to hold a sufficient proportion of either sewage or water in contact with a proper amount of air.

Smoke Abatement.

Whilst the sanitary engineer has done much to improve the surface conditions of our towns, to furnish clean water, and to remove our sewage, he has as yet done little to purify town air. Fog is caused by the floating particles of matter in the air becoming weighted with aqueous vapour; some particles, such as salts of ammonia or chloride of sodium, have a greater affinity for moisture than others. You will suffer from fog so long as you keep refuse stored in your towns to furnish ammonia, or so long as you allow your street surfaces to supply dust, of which much consists of powdered horse manure, or so long as you send the products of combustion into the atmosphere. Therefore, when you have adopted mechanical traction for your vehicles in towns you may largely reduce one cause of fog. And if you diminish your black smoke, you will diminish black fogs.

In manufactories you may prevent smoke either by care in firing, by using smokeless coal, or by washing the soot out of the products of consumption in its passage along the flue leading to the main chimney-shaft.

The black smoke from your kitchen may be avoided by the use of coke or of gas. But so long as we retain the hygienic arrangement of the open fire in our living rooms I despair of finding a fireplace, however well constructed, which will not be used in such a manner as to cause smoke, unless, indeed, the chimneys were reversed and the fumes drawn into some central shaft, where they might be washed before being passed into the atmosphere.

Electricity as a warming and cooking agent would be convenient, cleanly, and economical when generated by water power, or possibly wind power, but it is at present too dear when it has to be generated by means of coal. I can conceive, however, that our descendants may learn so to utilise electricity that they in some future century may be enabled by its means to avoid the smoke in their towns.

Mechanical Engineering.

In other branches of civil and mechanical engineering the reports in 1831 and 1832, on the state of this science, show that the theoretical and practical knowledge of the strength of timber had obtained considerable development; but in 1830, before the introduction of railways, cast-iron had been sparingly used in arched bridges for spans of from 160 to 200 feet, and wrought-iron had only been applied to large-span iron bridges on the suspension principle, the most notable instance of which was the Menai Suspension Bridge, by Telford. Indeed, whilst the strength of timber had been patiently investigated by engineers, the best form for the use of iron girders and struts was only beginning to attract attention, and the earlier volumes of our *Proceedings* contained numerous records of the researches of Eaton Hodgkinson, Barlow, Rennie, and others. It was not until twenty years later that Robert Stephenson and William Fairbairn erected the tubular bridge at Menai, followed by the more scientific bridge erected by Brunel at Saltash. These have now been entirely eclipsed by the skill with which the estuary of the Forth has been bridged with a span of 1700 feet, by Sir John Fowler and Sir Benjamin Baker.

The development of the iron industry is due to the association of the chemist with the engineer. The introduction of the hot blast by Neilson, in 1829, in the manufacture of cast-iron, had effected a large saving of fuel. But the chemical conditions which affect the strength and other qualities of iron, and its combinations with carbon, silicon, phosphorus, and other substances, had at that time scarcely been investigated.

In 1856 Bessemer brought before the British Association, at Cheltenham, his brilliant discovery for making steel direct from the blast furnace, by which he dispensed with the laborious process of first removing the carbon from pig-iron by puddling, and then adding by cementation the required proportion of carbon to make steel. This discovery, followed by Siemens's regenerative furnace, by Whitworth's compressed steel, and by the use of alloys, and by other improvements too numerous to mention here, have revolutionised the conditions under which metals are applied to engineering purposes.

Indeed, few questions are of greater interest, or possess more industrial importance, than those connected with metallic alloys. This is especially true of those alloys which contain the rarer metals; and the extraordinary effects of small quantities of chromium, nickel, tungsten, and titanium, on certain varieties of steel, have exerted profound influence on the manufacture of projectiles and on the construction of our armoured ships.

Of late years, investigations on the properties and structure of alloys have been numerous, and among the more noteworthy researches may be mentioned those of Dewar and Fleming on the distinctive behaviour, as regards the thermo-electric powers and electrical resistance, of metals and alloys at the very low temperatures which may be obtained by the use of liquid air.

Professor Roberts-Austen, on the other hand, has carefully studied the behaviour of alloys at very high temperatures, and by employing his delicate pyrometer has obtained photographic curves which afford additional evidence as to the existence of allotropic modifications of metals, and which have materially strengthened the view that alloys are closely analogous to saline solutions. In this connection it may be stated that the very accurate work of Heycock and Neville, on the lowering of the solidifying points of molten metals, which is caused by the presence of other metals, affords a valuable contribution to our knowledge.

Professor Roberts-Austen has, moreover, shown that the effect of any one constituent of an alloy upon the properties of the principal metal has a direct relation to the atomic volumes, and that it is consequently possible to foretell, in a great measure, the effect of any given combination.

A new branch of investigation, which deals with the micro-structure of metals and alloys, is rapidly assuming much importance. It was instituted by Sorby in a communication which he made to the British Association in 1864, and its development is due to many patient workers, among whom M. Osmond occupies a prominent place.

Metallurgical science has brought aluminium into use by cheapening the process of its extraction; and if by means of the wasted forces in our rivers, or possibly of the wind, the extraction be still further cheapened by the aid of electricity, we may not only utilise the metal or its alloys in increasing the spans of our bridges, and in affording strength and lightness in the construction of our ships, but we may hope to obtain a material which may render practicable the dreams of Icarus and of Maxim, and for purposes of rapid transit enable us to navigate the air.

Long before 1831 the steam-engine had been largely used on rivers and lakes, and for short sea passages, although the first Atlantic steam-service was not established till 1836.

As early as 1820 the steam-engine had been applied by Gurney, Hancock, and others to road traction. The absurd impediments placed in their way by road trustees, which, indeed, are still enforced, checked any progress. But the question of mechanical traction on ordinary roads was practically shelved in 1830, at the time of the formation of the British Association, when the locomotive engine was combined with a tubular boiler and an iron road on the Liverpool and Manchester Railway.

Great, however, as was the advance made by the locomotive engine of Robert Stephenson, these earlier engines

were only toys compared with the compound engines of to-day which are used for railways, for ships, or for the manufacture of electricity. Indeed, it may be said that the study of the laws of heat, which have led to the introduction of various forms of motive power, are gradually revolutionising all our habits of life.

The improvements in the production of iron, combined with the developed steam-engine, have completely altered the conditions of our commercial intercourse on land; whilst the changes caused by the effects of these improvements in ship-building, and on the ocean carrying trade, have been, if anything, still more marked.

The use of iron favours the construction of ships of a large size, of forms which afford small resistance to the water, and with compartments which make the ships practically unsinkable in heavy seas, or by collision. Their size, the economy with which they are propelled, and the certainty of their arrival cheapens the cost of transport.

The steam-engine, by compressing air, gives us control over the temperature of cool chambers. In these, not only fresh meat, but the delicate produce of the Antipodes, is brought across the ocean to our doors without deterioration.

Whilst railways have done much to alter the social conditions of each individual nation, the application of iron and steam to our ships is revolutionising the international commercial conditions of the world; and it is gradually changing the course of our agriculture, as well as of our domestic life.

But great as have been the developments of science in promoting the commerce of the world, science is asserting its supremacy even to a greater extent in every department of war. And perhaps this application of science affords at a glance, better than almost any other, a convenient illustration of the assistance which the chemical, physical, and electrical sciences are affording to the engineer.

The reception of warlike stores is not now left to the uncertain judgment of "practical men," but is confided to officers who have received a special training in chemical analysis, and in the application of physical and electrical science to the tests by which the qualities of explosives, of guns, and of projectiles can be ascertained.

For instance, take explosives. Till quite recently black and brown powders alone were used, the former as old as civilisation, the latter but a small modern improvement adapted to the increased size of guns. But now the whole family of nitro-explosives are rapidly superseding the old powder. These are the direct outcome of chemical knowledge; they are not mere chance inventions, for every improvement is based on chemical theories, and not on random experiment.

The construction of guns is no longer a haphazard operation. In spite of the enormous forces to be controlled and the sudden violence of their action, the researches of the mathematician have enabled the just proportions to be determined with accuracy; the labours of the physicist have revealed the internal conditions of the materials employed, and the best means of their favourable employment. Take, for example, Longridge's coiled-wire system, in which each successive layer of which the gun is formed receives the exact proportion of tension which enables all the layers to act in unison. The chemist has rendered it clear that even the smallest quantities of certain ingredients are of supreme importance in affecting the tenacity and trustworthiness of the materials.

The treatment of steel to adapt it to the vast range of duties it has to perform is thus the outcome of patient research. And the use of the metals—manganese, chromium, nickel, molybdenum—as alloys with iron has resulted in the production of steels possessing varied and extraordinary properties. The steel required to resist the conjugate stresses developed, lightning-fashion, in a gun necessitates qualities that would not be suitable in the projectile which that gun hurls with a velocity of some

2500 feet per second against the armoured side of a ship. The armour, again, has to combine extreme superficial hardness with great toughness, and during the last few years these qualities are sought to be attained by the application of the cementation process for adding carbon to one face of the plate, and hardening that face alone by rapid refrigeration.

The introduction of quick-firing guns from 0.303 (*i.e.*, about one-third) of an inch to 6-inch calibre has rendered necessary the production of metal cartridge-cases of complex forms drawn cold out of solid blocks or plate of the material; this again has taxed the ingenuity of the mechanic in the device of machinery, and of the metallurgist in producing a metal possessed of the necessary ductility and toughness. The cases have to stand a pressure at the moment of firing of as much as twenty-five tons to the square inch—a pressure which exceeds the ordinary elastic limits of the steel of which the gun itself is composed.

There is nothing more wonderful in practical mechanics than the closing of the breech openings of guns, for not only must they be gas-tight at these tremendous pressures, but the mechanism must be such that one man by a single continuous movement shall be able to open or close the breech of the largest gun in some ten or fifteen seconds.

The perfect knowledge of the recoil of guns has enabled the reaction of the discharge to be utilised in compressing air or springs by which guns can be raised from concealed positions in order to deliver their fire, and then made to disappear again for loading; or the same force has been used to run up the guns automatically immediately after firing, or, as in the case of the Maxim gun, to deliver in the same way a continuous stream of bullets at the rate of ten in one second.

In the manufacture of shot and shell cast-iron has been almost superseded by cast and wrought steel, though the hardened Palliser projectiles still hold their place. The forged-steel projectiles are produced by methods very similar to those used in the manufacture of metal cartridge-cases, though the process is carried on at a red heat and by machines much more powerful.

In every department concerned in the production of war-like stores electricity is playing a more and more important part. It has enabled the passage of a shot to be followed from its seat in the gun to its destination.

In the gun, by means of electrical contacts arranged in the bore, a time curve of the passage of the shot can be determined.

From this the mathematician constructs the velocity-curve, and from this, again, the pressures producing the velocity are estimated, and used to check the same indications obtained by other means. The velocity of the shot after it has left the gun is easily ascertained by the Boulangé apparatus.

Electricity and photography have been laid under contribution for obtaining records of the flight of projectiles and the effects of explosions at the moment of their occurrence. Many of you will recollect Mr. Vernon Boys' marvellous photographs showing the progress of the shot driving before it waves of air in its course.

Electricity and photography also record the properties of metals and their alloys as determined by curves of cooling.

The readiness with which electrical energy can be converted into heat or light has been taken advantage of for the firing of guns, which in their turn can, by the same agency, be laid on the object by means of range-finders placed at a distance and in advantageous and safe positions; while the electric light is utilised to illumine the sights at night, as well as to search out the objects of attack.

The compact nature of the glow-lamp, the brightness of the light, the circumstance that the light is not due to combustion, and therefore independent of air, facilitates the examination of the bore of guns, the insides of

shells, and other similar uses—just as it is used by a doctor to examine the throat of a patient.

(To be continued).

A REFORM IN CHEMICAL, PHYSICAL, AND TECHNICAL CALCULATIONS.

By C. J. HANSSEN, C.E.

(Continued from p. 103).

The external caloric work of steam, which is overcoming atmospheric or other outer resistance, and is able to do mechanical or dynamic work, is, pro 1 cbm. steam pro 1 atmosphere pressure, at any temperature = 24½ calors.
pro 1 kg. steam = $\frac{\text{absolute temperature}}{9}$; consequently—

$$\text{At } 219\frac{1}{2}^{\circ} \text{ absol.} \quad \dots \dots = \frac{219\frac{1}{2}}{9} = 24\frac{1}{2} \text{ calors.}$$

$$\text{At } 273^{\circ} \quad \dots \dots = \frac{273}{9} = 30\frac{1}{2} \quad "$$

$$\text{At } 373^{\circ} \quad \dots \text{ (1 atmosph.)} = \frac{373}{9} = 41\frac{1}{2} \quad "$$

$$\text{At } 454^{\circ} \quad \dots \text{ (10 atmosph.)} = \frac{454}{9} = 50\frac{1}{2} \quad "$$

The product of absolute pressure $\times$ volume per kg. ($V \times P$) increases in direct ratio to the absolute temperature of steam, as shown by the diagonal straight V P line in the diagram.

Combustion.

When a substance is burnt we feel the heat produced, and see flames and light emit from the burning object, and we have been thus led to imagine that it is the visible object only which burns, and the heat developed in the process of burning we commonly consider to be the quantity of heat which the burning substance—for instance, 1 kg. of coal—is able to produce; we may, however, just as well reverse the case, and consider the heat developed in the process of combustion as produced by combining a certain quantity of oxygen with the burning substance, and measure the heat produced by the quantity of oxygen which combines with the burning substance.

All substances combine with other substances in simple definite proportions, and this rule also holds good in the chemical process termed combustion; we may therefore be sure that 1 kg. of oxygen, when combining with any other substance, *always will produce the same quantity of heat*, just as well as 1 kg. of carbon, if in combustion or by any other chemical process combined with oxygen, always produces a certain and definite quantity of heat. If experience in some cases seems to contradict this rule, and apparently gives different results, this can only be caused by imperfections in the method and apparatus used in the research, and such anomalies will by-and-by be found out and corrected.

Of all substances at our disposal, capable of producing heat, carbon, hydrogen, and oxygen are the most generally applicable; and a correct determination of the value of their compounds as producers of heat will therefore be of the highest importance for science and industry, but as yet the chief authorities disagree on this subject.

The quantity of heat produced by combustion of 1 kg. of hydrogen of 273° absolute, with 8 kg. of oxygen of the same temperature, is found by—

	Calors.
Andrews	= 33881
Humphrys	= 34722
Favre and Silbermann ..	= 34462
Dulong	= 34742
Thomsen	= 34181
Fischer	= 34384
Berthelot	= 34600

The vapour produced condensed to liquid water of 0° N = 273° absolute.

and the quantity of heat produced by combustion of 1 kg. of carbon monoxide with oxygen is found by—

Favre and Silbermann ..	= 2403 calors.
Dulong	= 2489 "
Fischer	= 2440 "
Ferguson Bell	= 2444 "
Humphrys	= 2489 "

As not two of these agree, it seems evident that all are more or less erroneous.

The author has shown (CHEMICAL NEWS, lxxii., p. 8) that 1 kg. hydrogen of 0° N (273° N absol.) burnt with 8 kg. oxygen, and the product of combustion condensed to the initial temperature of the components, produces 34679.70 calors., which in all following calculations is rounded off to 34680 calors.

This figure, being the mean of Messrs. Humphrys, Favre and Silbermann's, Dulong, and Berthelot's determinations, the author considers to be a correct standard, from which the heating power of other substances may be calculated, and consequently we find that—

1 cbm. of hydrogen of atmospheric density and 0° N, which weighs $\frac{1}{16}$ kg., will produce $34680 \times \frac{1}{16} = 3096\frac{1}{2}$ calors.; that—

1 kg. of oxygen will produce $\frac{34680}{8} = 4335$ calors., and—

1 cbm. of oxygen of atm. density and 0° N $-4335 \times \frac{1}{16} = 6192\frac{1}{2}$ calors., and 1 litre oxygen $\frac{6192\frac{1}{2}}{1000} = 6\frac{1}{2}\frac{1}{10}$ calors.; and further—

1 kg. of aeriform carbon, burning with 1 $\frac{1}{2}$ kg. oxygen, will produce $4335 \times 1\frac{1}{2} = 5780$ calors., forming 2 $\frac{1}{2}$ kg. CO.

1 cbm. of aeriform carbon (atmospheric density and 0° N), burnt with 1 cbm. oxygen of equal density and temperature, will produce $6192\frac{1}{2}$ cal. $\times$ 1 cbm. O $= 6192\frac{1}{2}$ calors., forming 2 cbm. CO.

1 kg. of aeriform carbon, burning with 2 $\frac{3}{8}$ kg. oxygen, will produce $4335 \times 2\frac{3}{8} = 11560$ calors., forming 3 $\frac{3}{8}$ kg. CO₂; and—

1 cbm aeriform carbon, burning with 2 cbm. oxygen, will produce $6192\frac{1}{2}$ cal. $\times$ 2 = 12385 $\frac{1}{2}$ calors., forming 2 cbm. CO₂.

1 kg. of carbon monoxide, which contains $\frac{1}{2}$ kg. of aeriform carbon, burning with $\frac{1}{2}$ kg. oxygen, will produce $\frac{1}{2} \times 4335$ cal. = 2167 $\frac{1}{2}$ calors., forming 1 $\frac{1}{2}$ kg. CO₂; and—

1 cbm. of carbon monoxide, which contains $\frac{1}{2}$ cbm. of aeriform carbon, burning with $\frac{1}{2}$ cbm. oxygen, will produce $6192\frac{1}{2} \times \frac{1}{2} = 3096\frac{1}{2}$ calors., forming 1 cbm. CO₂.

The heat produced by 1 kg. pure fixed carbon, burnt with 1 $\frac{1}{2}$ kg. oxygen to CO, and with 2 $\frac{3}{8}$ kg. O to CO₂, is given differently by various authorities; but the mean of their results is $\frac{1}{2}$ of the heat produced by burning aeriform carbon; and this leads to the following simple relation:—

1 kg. of aeriform carbon, burnt to CO₂, produces sensible heat = 11560 calors.
1 kg. of solid carbon produces likewise 11560 calors., but in gasifying the fixed carbon $\frac{1}{2} \times 11560$ become latent .. = 3302 $\frac{1}{2}$ "

And only $\frac{1}{2} \times 11560$ cal. = 8257 $\frac{1}{2}$ " are set free as sensible heat.

1 kg. of solid carbon, burnt to CO, produces $\frac{1}{2} \times 11560$ cal. = 5780 calors.
In gasifying become latent = 3302 $\frac{1}{2}$ "

And the sensible heat produced is .. = 2477 $\frac{1}{2}$ "

Combustion of Hydrocarbons.

If hydrocarbon gases burn with oxygen or air the case is different, because the compound must be decomposed before its components can unite with the oxygen to form the new compounds CO₂ and H₂O.

Decomposing a hydrocarbon gas, or separating the hydrogen contained in it from the carbon, by the united action of heat and the chemical affinity of oxygen, will absorb half the heat produced by the H in the hydrocarbon; consequently is absorbed or becoming latent:—
Pro 1 cbm. H of atm. density and 0° N (273° absol.)—

$$\frac{3096\frac{1}{2} \text{ cal.}}{2} = 1548\frac{1}{4} \text{ calors.}$$

and pro 1 kg. H—

$$\frac{34680 \text{ cal.}}{2} = 17340 \text{ calors.}$$

We find thus, the products of combustion being cooled down to 0° N (273° N absol.), that—

1 cbm. methane of 1 atm. and 273° N absol., burnt with 2 cbm. oxygen, produces
 $2 \times 6192\frac{1}{2}$ cal. = 12385 $\frac{1}{2}$ calors.
Separating 2 cbm. H from C absorbs
 $2 \times 1548\frac{1}{4}$ cal. = 3096 $\frac{1}{2}$ "

Consequently 1 cbm. methane produces sensible heat = 9289 $\frac{1}{2}$ " or exactly $\frac{1}{2}$ of what would be due for the 2 cbm. O burnt with it.

1 kg. methane, burnt with 4 kg. O, produces
 4×4335 cal. = 17340 calors.
Separating $\frac{1}{2}$ kg. H from C absorbs
 $\frac{1}{2} \times 17340$ cal. = 4335 "

Consequently 1 kg. methane produces sensible heat = 13005 " Or likewise $\frac{1}{2}$ of what would be due to the 4 kg. O consumed, while $\frac{1}{2}$ of the heat actually produced becomes latent.

In a similar way we find the sensible heat produced by combustion of the total heat due to the O.

1 cbm. .. burnt with Cbm. O.	Sensible heat. Calors.	1 kg. burnt with Kg. O.	Sensible heat. Calors.	Sensib.	Latent.
Acetylene .. 2 $\frac{1}{2}$	13933 $\frac{1}{2}$	3 $\frac{1}{2}$	12004 $\frac{1}{2}$	9/10	1/10
Ethylene .. 3	15482 $\frac{1}{2}$	3 $\frac{1}{2}$	12385 $\frac{1}{2}$	5/6	1/6
Ethane .. 3 $\frac{1}{2}$	17030 $\frac{1}{2}$	3 $\frac{1}{2}$	12716	11/14	3/14
Allylene .. 4	21685	3 $\frac{1}{2}$	12138	7/8	1/8
Propylene .. 4 $\frac{1}{2}$	23223 $\frac{1}{2}$	3 $\frac{1}{2}$	12385 $\frac{1}{2}$	5/6	1/6
Propane .. 5	24771 $\frac{1}{2}$	3 $\frac{1}{2}$	12610 $\frac{1}{2}$	4/5	1/5
Butylene .. 6	30964 $\frac{1}{2}$	3 $\frac{1}{2}$	12385 $\frac{1}{2}$	5/6	1/6
Butane .. 6 $\frac{1}{2}$	32512 $\frac{1}{2}$	3 $\frac{1}{2}$	12556 $\frac{1}{2}$	21/26	5/26
Pentane .. 8	40253 $\frac{1}{2}$	3 $\frac{1}{2}$	12523 $\frac{1}{2}$	25/32	7/32
Benzene gas 7 $\frac{1}{2}$	41801 $\frac{1}{2}$	3 $\frac{1}{2}$	12004 $\frac{1}{2}$	9/10	1/10

Combustion of Mixed Gases.

Coal gas, 17 candles, 1 cbm. atm. density, 273° N absolute:—

Contains litres	Requires oxygen Litres.	Produces sensible heat equal to Litres O.
Methane .. 370.0 $\times$ 2	= 740.0	740.0 $\times$ $\frac{1}{2}$ = 555.00
Ethylene .. 25.0 $\times$ 3	= 75.0	75.0 $\times$ $\frac{1}{2}$ = 62.50
Propylene .. 12.0 $\times$ 4 $\frac{1}{2}$	= 54.0	54.0 $\times$ $\frac{1}{2}$ = 45.00
Benzene .. 13.0 $\times$ 7 $\frac{1}{2}$	= 97.5	97.5 $\times$ $\frac{1}{2}$ = 87.75
Carbon monoxide 52.5 $\times$ $\frac{1}{2}$	= 26.25	26.25
Hydrogen .. 490.0 $\times$ $\frac{1}{2}$	= 245.0	245.00
Carbon dioxide 4.0	1237.75	
Nitrogen .. 32.5		
Oxygen .. 1.0	1.00	1.00

1 cbm. gas = 1000.0 requires 1236.75 O, of which 1032.50 litres O only produce sensible heat, and develop—

$$1036.5 \times \frac{867}{140} = 6332.196 \text{ calors. sensible heat.}$$

One cbm. of this gas weighs 5853/11200 kg.; 1 kg. therefore contains 11200/5853 cbm., will for combustion

require 2.36565 cbm. O = 3.3795 kg. O, and will produce 12116.965 calors. of sensible heat.

Water Gas, H + CO.—This mixed gas, which consists of equal volumes of H and CO, is formed when steam passes through glowing carbon; the H of the steam is set free, and the O combines with C, forming CO.

One kg. steam of 100° (373° N absol.) consists of 1/9 kg. H and 8/9 kg. O, and forms when passed through glowing carbon, and the product cooled down to 0° N, at atmospheric density; 1/9 kg. = 56/45 cbm. H; 8/9 kg. O combines with 6/9 kg. C, forming 14/9 kg. = 56.45 cbm. CO; consequently 1 kg. steam and 6/9 kg. C form 15/9 kg. = 112/45 cbm. water gas of 0° N (273° N absol.) and atm. density; consequently—

1 kg. water gas = 112/75 cbm., and 1 cbm. = 75/112 kg. 1 kg. water gas contains 3/5 kg. steam + 2/5 kg. C.

1 kg. water gas contains 1/15 kg. H + 14/15 CO; = 56.75 cbm. H + 56.75 cbm. CO.

1 cbm. water gas contains 1/5 cbm. H + 4/5 cbm. CO; = 5/112 kg. H + 5/8 kg. CO.

Production of 1 kg. of water gas of 273° N. absol. requires:—

3/5 kg. of liquid water of 273° N absol. dissolved into H and O by the united action of heat and the chemical affinity of carbon, absorbs, separating 1/15 kg. H from O, 1/15 × 17340 cal. = 1156 calors.

2/5 kg. solid carbon to gasify absorbs 2/5 × 3302½ cal. = 1321½ "

2477½ "

2/5 kg. C, burnt with 8/15 kg. O. to form 14/15 kg. CO, produces 8/15 × 4335 cal. = 2312 "

1 kg. water gas requires for its production = 165½ "

1 cbm. of atm. density requires 165½ × 75/112 kg. = 110½ calors.

Combustion of 1 kg. of Water Gas.

For 1/15 kg. H is required 8/15 kg. O } 16/15 kg. O, which
" 14/15 " CO " 8/15 " O } produces 4624 calors.

Combustion of 1 cbm. Water Gas.

For 1/2 cbm. H is required 1/4 cbm. O } 1/2 cbm. O, which
" 1/2 " CO " 1/4 " O } produces 3096½ calors.

(To be continued).

3, Valdemarsgade, Copenhagen, V.
July 27, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Zeitschrift für Anorganische Chemie,
Vol. viii., Parts 1 and 2.

The Atomic and Molecular Solution Volumes.—J. Traube.—This extensive paper has been already noticed.

The Foundations of a New System of the Elements.—J. Traube.—Already inserted.

Critical Studies on the Chemistry of Titanium.—E. A. Schneider.—The results of the above studies may be briefly summarised as—1. The product obtained from potassium titanate-fluoride by reduction with sodium in a current of hydrogen contains not only oxygen, but also hydrogen. Whether we have here a titanium hydride, hydroxide, or a case of simple absorption, cannot

be decided until chemically pure titanium has been obtained. 2. The assumption that this reduction-product consists exclusively of a lower stage of oxidation of titanium is opposed to the following facts:—a. No such lower oxides of titanium have been hitherto isolated. b. The melting-point of titanium lies at a very high temperature, as may be learnt from the difficulty of alloying it with copper. 3. There are probably two titanium nitrides. The higher, indigo-blue nitride, passes at a white-heat into the lower and more stable bronze-yellow nitride. 4. The higher nitride can be easily converted into a crystalline titanium sulphide by heating to redness with sulphur in a current of hydrogen. 5. A "titanium chloroform" has not yet proved obtainable. In this respect titanium behaves like tin. On the action of dry hydrochloric acid upon elementary titanium there arises a chlorinised product, not volatile. It must be kept in mind that this reaction may depend upon the presence of a titanium hydroxide or a solid titanium hydride in the elementary titanium.

The Influence of Hydration upon Solubility.—N. Kurnakow.—This paper requires the two accompanying diagrams.

The Solutions of Green Chromium Chloride, CrCl₃.6H₂O.—A. Piccini.—The inferences following from the author's results are:—Silver fluoride has, in reference to the green chromium chloride, the property of precipitating that portion of chlorine—or causing it to assume the function of an ion—which is not precipitable by the other silver salts, and in their presence does not act as an ion. In solutions in which the method of the boiling-point indicates little or no dissociation of the green chromium chloride, all the chlorine is precipitated by silver nitrate, whilst in solutions in which dissociation ensues the precipitation is only partial. The solutions of green chromium chloride in methylic alcohol take, in presence of silver nitrate, an intermediate position between the watery solutions and those on ethylic alcohol.

On some New Methods of obtaining Platinous Chlorides, and on the Probable Existence of Platinum Subchloride.—M. Carey Lea.

The Cæsium Double Chlorides, Bromides, and Iodides, with Cobalt and Nickel.—G. F. Campbell.

It is understood that these two papers have appeared also in the English languages.

ACETONE—Answering all requirements.

- ACID ACETIC—Purest and sweet.
- BORACIC—Cryst. and powder.
- CITRIC—Cryst. made in earthenware.
- GALLIC—From best Chinese galls, pure.
- SALICYLIC—By Kolbe's process.
- TANNIC—For Pharmacy and the Arts.

LIQUID CHLORINE

(Compressed in steel cylinders).

FORMALIN (40% CH₂O)—Antiseptic and Preservative.

POTASS. PERMANGANATE—Cryst., large and small.

SULPHOCYANIDE OF AMMONIUM.

BARIUM.

POTASSIUM.

TARTAR EMETIC—Cryst. and Powder.

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THE CHEMICAL NEWS.

VOL. LXXII., No. 1869.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

IPSWICH, 1895.

INAUGURAL ADDRESS OF THE PRESIDENT,
SIR DOUGLAS GALTON, K.C.B., D.C.L., F.R.S.

(Concluded from p. 136).

INFLUENCE OF INTERCOMMUNICATION AFFORDED BY BRITISH ASSOCIATION ON SCIENCE PROGRESS.

THE advances in engineering have produced the steam-engine, the railway, the telegraph, as well as our engines of war, may be said to be the result of commercial enterprise rendered possible only by the advances which have taken place in the several branches of science since 1831. Having regard to the intimate relations which the several sciences bear to each other, it is abundantly clear that much of this progress could not have taken place in the past, nor could further progress take place in the future, without intercommunication between the students of different branches of science.

The founders of the British Association based its claims to utility upon the power it afforded for this intercommunication. Mr. Vernon Harcourt (the uncle of your present General Secretary), in the address he delivered in 1832, said:—"How feeble is man for any purpose when he stands alone—how strong when united with other men!"

I claim for the British Association that it has fulfilled the objects of its founders, that it has had a large share in promoting intercommunication and combination.

Our meetings have been successful because they have maintained the true principles of scientific investigation. We have been able to secure the continued presence and concurrence of the master-spirits of science. They have been willing to sacrifice their leisure, and to promote the welfare of the Association, because the meetings have afforded them the means of advancing the sciences to which they are attached.

The Association has, moreover, justified the views of its founders in promoting intercourse between the pursuers of science, both at home and abroad, in a manner which is afforded by no other agency.

The weekly and sessional reunions of the Royal Society, and the annual *soirées* of other scientific societies, promote this intercourse to some extent; but the British Association presents to the young student, during its week of meetings, easy and continuous social opportunities for making the acquaintance of leaders in science, and thereby obtaining their directing influence.

It thus encourages, in the first place, opportunities of combination, but, what is equally important, it gives at the same time material assistance to the investigators whom it thus brings together.

The reports on the state of science at the present time, as they appear in the last volume of our *Proceedings*, occupy the same important position, as records of science progress, as that occupied by those Reports in our earlier years. We exhibit no symptom of decay.

SCIENCE IN GERMANY FOSTERED BY THE STATE AND MUNICIPALITIES.

Our neighbours and rivals rely largely upon the guidance of the State for the promotion of both science teaching

and of research. In Germany the foundations of technical and industrial training are laid in the *Realschulen*, and supplemented by the Higher Technical Schools. In Berlin that splendid institution, the Royal Technical High School, casts into the shade the facilities for education in the various Polytechnics which we are now establishing in London. Moreover, it assists the practical workman by a branch department, which is available to the public for testing building materials, metals, paper, oil, and other matters. The standards of all weights and measures used in trade can be purchased from or tested by the Government Department for Weights and Measures.

For developing pure scientific research and for promoting new applications of science to industrial purposes the German Government at the instance of von Helmholtz, and aided by the munificence of Werner von Siemens, created the *Physikalische Technische Reichsanstalt* at Charlottenburg.

This establishment consists of two divisions. The first is charged with pure research, and is at the present time engaged in various thermal, optical, and electrical, and other physical investigations. The second branch is employed in operations of delicate standardising to assist the wants of research students—for instance, dilatation, electrical resistances, electric and other forms of light, pressure gauges, recording instruments, thermometers, pyrometers, tuning-forks, glass, oil-testing apparatus, viscosity of glycerin, &c.

Dr. Kohlrausch succeeded Helmholtz as president, and takes charge of the first division. Professor Hagen, the director under him, has charge of the second division. A professor is in charge of each of the several sub-departments. Under these are various subordinate posts, held by younger men, selected for previous valuable work, and usually for a limited time.

The general supervision is under a Council, consisting of a president, who is a Privy Councillor, and twenty-four members, including the president and director of the *Reichsanstalt*; of the other members about ten are professors or heads of physical and astronomical observatories connected with the principal universities in Germany. Three are selected from leading firms in Germany representing mechanical, optical, and electric science, and the remainder are principal scientific officials connected with the Departments of War and Marine, the Royal Observatory at Potsdam, and the Royal Commission for Weights and Measures.

This Council meets in the winter, for such time as may be necessary, for examining the research work done in the first division during the previous year, and for laying down the scheme for research for the ensuing year; as well as for suggesting any requisite improvements in the second division. As a consequence of the position which science occupies in connection with the State in Continental countries, the services of those who have distinguished themselves either in the advancement or in the application of science are recognised by the award of honours; and thus the feeling for science is encouraged throughout the nation.

ASSISTANCE TO SCIENTIFIC RESEARCH IN GREAT BRITAIN.

Great Britain maintained for a long time a leading position among the nations of the world by virtue of the excellence and accuracy of its workmanship, the result of individual energy; but the progress of mechanical science has made accuracy of workmanship the common property of all nations of the world. Our records show that hitherto, in its efforts to maintain its position by the application of science and the prosecution of research, England has made marvellous advances by means of voluntary effort, illustrated by the splendid munificence of such men as Cassiot, Joseph Whitworth, James Mason, and Ludwig Mond; and, whilst the increasing field of scientific research compels us occasionally to seek for

Government assistance, it would be unfortunate if by any change voluntary effort were fettered by State control.

The following are the principal voluntary agencies which help forward scientific research in this country:—The Donation Fund of the Royal Society, derived from its surplus income. The British Association has contributed £60,000 to aid research since its formation. The Royal Institution, founded in the last century, by Count Rumford, for the promotion of research, has assisted the investigations of Davy, of Young, of Faraday, of Frankland, of Tyndall, of Dewar, and of Rayleigh. The City Companies assist scientific research and foster scientific education both by direct contributions and through the City and Guilds Institute. The Commissioners of the Exhibition of 1881 devote £6000 annually to science research scholarships, to enable students who have passed through a college curriculum and have given evidence of capacity for original research to continue the prosecution of science, with a view to its advance or to its application to the industries of the country. Several scientific societies have promoted direct research, each in their own branch of science, out of their surplus income; and every scientific society largely assists research by the publication, not only of its own proceedings, but often of the work going on abroad in the branch of science which it represents.

The growing abundance of matter year by year increases the burden thus thrown on their finances, and the Treasury has recently granted to the Royal Society £1000 a year, to be spent in aid of the publication of scientific papers not necessarily limited to those of that Society.

The Royal Society has long felt the importance to scientific research of a catalogue of all papers and publications relating to pure and applied science, arranged systematically both as to authors' names and as to subject treated, and the Society has been engaged for some time upon a catalogue of that nature. But the daily increasing magnitude of these publications, coupled with the necessity of issuing the catalogue with adequate promptitude and at appropriate intervals, renders it a task which could only be performed under International co-operation. The officers of the Royal Society have therefore appealed to the Government to urge Foreign Governments to send delegates to a Conference to be held next July to discuss the desirability and the scope of such a catalogue, and the possibility of preparing it.

The universities and colleges distributed over the country, besides their function of teaching, are large promoters of research, and their voluntary exertions are aided in some cases by contributions from Parliament in alleviation of their expenses.

Certain executive departments of the Government carry on research for their own purposes, which in that respect may be classed as voluntary. The Admiralty maintains the Greenwich Observatory, the Hydrographical Department, and various experimental services; and the War Office maintains its numerous scientific departments. The Treasury maintains a valuable chemical laboratory for Inland Revenue, Customs, and agricultural purposes. The Science and Art Department maintains the Royal College of Science, for the education of teachers and students from elementary schools; it allows the scientific apparatus in the National Museum to be used for research purposes by the professors. The Solar Physics Committee, which has carried on numerous researches in solar physics, was appointed by and is responsible to this Department. The Department also administers the Sir Joseph Whitworth engineering research scholarships. Other scientific departments of the Government are aids to research, as, for instance, the Ordnance and the Geological Surveys, the Royal Mint, the Natural History Museum, Kew Gardens, and other lesser establishments in Scotland and Ireland; to which may be added, to some extent, the Standards Department of the Board of Trade, as well as municipal museums, which are gradually spreading over the country.

For direct assistance to voluntary effort the Treasury contributes £4000 a year to the Royal Society for the promotion of research, which is administered under a board whose members represent all branches of Science. The Treasury, moreover, contributes to marine biological observatories, and in recent years has defrayed the cost of various expeditions for biological and astronomical research, which in the case of the *Challenger* expedition involved very large sums of money.

In addition to these direct aids to science, Parliament, under the Local Taxation Act, handed over to the County Councils a sum, which amounted in the year 1893 to £615,000, to be expended on technical education. In many country districts, so far as the advancement of real scientific technical progress in the nation is concerned, much of this money has been wasted for want of knowledge. And whilst it cannot be said that the Government or Parliament have been indifferent to the promotion of scientific education and research, it is a source of regret that the Government did not devote some small portion of this magnificent gift to affording an object-lesson to County Councils in the application of science to technical instruction, which would have suggested the principles which would most usefully guide them in the expenditure of this public money.

Government assistance to science has been based mainly on the principle of helping voluntary effort. The Kew Observatory was initiated as a scientific observatory by the British Association. It is now supported by the Gassiot trust fund, and managed by the Kew Observatory Committee of the Royal Society. Observations on magnetism, on meteorology, and the record of sun-spots, as well as experiments upon new instruments for assisting meteorological, thermometrical, and photographic purposes, are being carried on there. The Committee has also arranged for the verification of scientific measuring instruments, the rating of chronometers, the testing of lenses and of other scientific apparatus. This institution carries on to a limited extent some small portion of the class of work done in Germany by that magnificent institution, the Reichsanstalt at Charlottenburg, but its development is fettered by want of funds. British students of science are compelled to resort to Berlin and Paris when they require to compare their more delicate instruments and apparatus with recognised standards. There could scarcely be a more advantageous addition to the assistance which Government now gives to science than for it to allot a substantial annual sum to the extension of the Kew Observatory, in order to develop it on the model of the Reichsanstalt. It might advantageously retain its connection with the Royal Society, under a Committee of Management representative of the various branches of science concerned, and of all parts of Great Britain.

CONCLUSION.

The various agencies for scientific education have produced numerous students admirably qualified to pursue research; and at the same time almost every field of industry presents openings for improvement through the development of scientific methods. For instance, agricultural operations alone offer openings for research to the biologist, the chemist, the physicist, the geologist, the engineer, which have hitherto been largely overlooked. If students do not easily find employment, it is chiefly attributable to a want of appreciation for science in the nation at large.

This want of appreciation appears to arise from the fact that those who nearly half a century ago directed the movement of national education were trained in early life in the universities, in which the value of scientific methods was not at that time fully recognised. Hence our elementary, and even our secondary and great public schools, neglected for a long time to encourage the spirit of investigation which develops originality. This defect is diminishing daily.

There is, however, a more intangible cause which may

have had influence on the want of appreciation of science by the nation. The Government, which largely profits by science, aids it with money, but it has done very little to develop the national appreciation for science by recognising that its leaders are worthy of honours conferred by the State. Science is not fashionable, and science students—upon whose efforts our progress as a nation so largely depends—have not received the same measure of recognition which the State awards to services rendered by its own officials, by politicians, and by the Army and by the Navy, whose success in future wars will largely depend on the effective applications of science.

The Reports of the British Association afford a complete chronicle of the gradual growth of scientific knowledge since 1831. They show that the Association has fulfilled the objects of its founders in promoting and disseminating a knowledge of science throughout the nation.

The growing connection between the sciences places our annual meeting in the position of an arena where representatives of the different sciences have the opportunity of criticising new discoveries and testing the value of fresh proposals, and the Presidential and Sectional Addresses operate as an annual stock-taking of progress in the several branches of science represented in the Sections. Every year the field of usefulness of the Association is widening. For, whether with the geologist we seek to write the history of the crust of the earth, or with the biologist to trace out the evolution of its inhabitants, or whether with the astronomer, the chemist, and the physicist we endeavour to unravel the constitution of the sun and the planets or the genesis of the nebulae and stars which make up the universe, on every side we find ourselves surrounded by mysteries which await solution. We are only at the beginning of work.

I have, therefore, full confidence that the future records of the British Association will chronicle a still greater progress than that already achieved, and that the British nation will maintain its leading position amongst the nations of the world, if it will energetically continue its voluntary efforts to promote research, supplemented by that additional help from the Government, which ought never to be withheld when a clear case of scientific utility has been established.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION. IPSWICH, 1895.

By Prof. RAPHAEL MELDOLA, F.R.S., F.I.C., For. Sec. C.S.,
President of the Section.

THE STATE OF CHEMICAL SCIENCE IN 1851.

IN order to estimate the progress of chemical science since the year 1851, when the British Association last met in this town, it will be of interest for us to endeavour to place ourselves in the position of those who took part in the proceedings of Section B on that occasion. Perhaps the best way of performing this retrograde feat will be to confront the fundamental doctrines of modern chemistry with the state of chemical theory at that period, because at any point in the history of a science the theoretical conceptions in vogue—whether these conceptions have survived to the present time or not—may be taken as the abstract summation of the facts, *i.e.*, of the real and tangible knowledge existing at the period chosen as the standard of reference.

Without going too far back in time I may remind you that in 1811 the atomic theory of the chemists was grafted on to the kindred science of physics through the enunciation of the law associated with the name of Avogadro di Quaregna. The rationalising of this law had been accomplished in 1845; but the kinetic theory of gases, which had been foreshadowed by D. Bernoulli in

1738, and in later times by Herapath, Joule, and Krönig, lay buried in the archives of the Royal Society until recently unearthed by Lord Rayleigh and given to the world in 1892 under the authorship of Waterston, the legitimate discoverer. The later developments of this theory did not take place till after the last Ipswich meeting, *viz.*, in 1857—1862, by Clausius, and by Clerk Maxwell in 1860—1867. Thus the kinetic theory of gases of the physicists had not in 1851 acquired the full significance for chemists which it now possesses; the hypothesis of Avogadro was available, analogous conceptions had been advanced by Davy in 1812, and by Ampère in 1814; but no substantial chemical reasons for its adoption were adduced until the year 1846, when Laurent published his work on the law of even numbers of atoms and the nature of the elements in the free state (*Ann. Chim. Phys.* [3], xviii., 266).

The so called "New Chemistry," with which students of the present time are familiar, was, in fact, being evolved about the period when the British Association last assembled at Ipswich; but it was not till some years later, and then chiefly through the writings of Laurent and Gerhardt, that the modern views became accepted. It is of interest to note in passing that the nomenclature of organic compounds formed the subject of a report by Dr. Daubeny at that meeting, in which he says:—"It has struck me as a matter of surprise that none of the British treatises on Chemistry with which I am acquainted should contain any rules to guide us, either in affixing names to substances newly discovered or in divining the nature and relations of bodies from the appellations attached to them. Nor do I find this deficiency supplied in a manner which to me appears satisfactory when I turn to the writings of Continental chemists." In a subsequent portion of the report Dr. Daubeny adds:—"No name ought, for the sake of convenience, to exceed in length six or seven syllables." I am afraid the requirements of modern organic chemistry have not enabled us to comply with this condition.

Among other physical discoveries which have exerted an important influence on chemical theory, the law of Dulong and Petit, indicating the relationship between specific heat and atomic weight, had been announced in 1819, had been subsequently extended to compounds by Neumann, and still later had been placed upon a sure basis by the classical researches of Regnault in 1839. But here, again, it was not till after 1851 that Cannizzaro (1858) gave this law the importance which it now possesses in connection with the determination of atomic weights. Thermo-chemistry as a distinct branch of our science may also be considered to have arisen since 1851, although the foundations were laid before this period by the work of Favre and Silbermann, Andrews, Graham, and especially Hess, whose important generalisation was announced in 1840, and whose claim to just recognition in the history of physical chemistry has been ably advocated in recent times by Ostwald. But the elaboration of thermochemical facts and views in the light of the dynamical theory of heat was first commenced in 1853 by Julius Thomsen, and has since been carried on concurrently with the work of Berthelot in the same field which the latter investigator entered in 1865. Electro-chemistry in 1851 was in an equally rudimentary condition. Davy had published his electro-chemical theory in 1807, and in 1812 Berzelius had put forward those views on electric affinity which became the basis of his dualistic system of formulation. In 1833 Faraday announced his famous law of electro-chemical equivalence, which gave a fatal blow to the conception of Berzelius, and which later (1839—1840) was made use of by Daniell in order to show the untenability of the dualistic system. By 1851 the views of Berzelius had been abandoned, and, so far as chemical theory is concerned, the whole subject may be considered to have been in abeyance at that time. It is of interest to note, however, that in that year Williamson advanced, on quite distinct grounds, his now well-known theory of

atomic interchange between molecules, which theory in a more extended form was developed independently from the physical side and applied to electrolytes by Clausius in 1857. The modern theory of electrolysis associated with the names of Arrhenius, van't Hoff, and Ostwald, is of comparatively recent growth. It appears that Hittorf, in 1878, was the first to point out the relationship between electrolytic conductivity and chemical activity, this same author as far back as 1856 having combated the prevailing view that the electric current during electrolysis does the work of overcoming the affinities of the ions. Arrhenius formulated his theory of electrolytic dissociation in 1887, Planck having almost simultaneously arrived at similar views on other grounds.

Closely connected with electrolysis is the question of the constitution of solutions, and here again a convergence of work from several distinct fields has led to the creation of a new branch of physical chemistry which may be considered a modern growth. The relationship between the strength of a solution and its freezing-point had been discovered by Blagden towards the end of the last century, but in 1851 chemists had no notion that this observation would have any influence on the future development of their science. Another decade elapsed before the law was re-discovered by Rudorff (1861), and ten years later was further elaborated by de Coppet. Raoult published his first work on the freezing-point of solutions in 1880, and two years later the relationship between osmotic pressure and the lowering of freezing-point was established by H. de Vries, who first approached the subject as a physiologist, through observations on the cell-contents of living plants. As the work done in connection with osmotic pressure has had such an important influence on the "dissociation" theory of solutions, it will be of interest to note that at the last Ipswich meeting Thomas Graham made a communication on liquid diffusion, in which he "gave a view of some of the unpublished results, to ascertain whether solutions of saline bodies had a power of diffusion among liquids, especially water." In 1877 Pfeffer, who, like de Vries, entered the field from the botanical physiological side, succeeded in effecting the measurement of osmotic pressure. Ten years later van't Hoff formulated the modern dissociation theory of solution by applying to dissolved substances the laws of Boyle, Gay Lussac, and Avogadro, the law of osmotic pressure, and Raoult's law connecting the depression of freezing point with molecular weight, thus laying the foundation of a doctrine which, whether destined to survive in its present form or not, has certainly exerted a great influence on contemporary chemical thought.

Another, further, the state of knowledge in 1851 concerning such leading principles as dissociation or thermodynamic action and chemical equilibrium. Abnormal vapour densities had been observed by Avogadro in 1811, and by Ampère in 1814. Grove had dissociated water vapour by heat in 1847, but the first great advance was made ten years later by Sainte-Claire Deville, from whose work has emanated our existing knowledge of this subject. I may add that the application of this principle to explain the cases of abnormal vapour density was made in 1855 by Boppé, Kekulé, and Cannizzaro, almost simultaneously; but, strangely enough, this explanation was accepted by Deville himself. The subsequent stages are subjects of modern history. The current views on mass action were foreshadowed, as is well known, by Berthollet in his "Statique Chimique," published in 1803, but no great advance had been made when the British Association last met here. The subject first began to assume a quantitative aspect through the researches of Bunsen and Gladstone in 1853, and was much advanced by Gladstone in 1863, and by Harcourt and Reaon a year later. Goldberg and Waage published their classical work on this subject in 1867.

Equally striking will appear the advances made since 1851 if we consider that the whole subject of spectrum analysis, which brings out science into relationship with

astronomy, has been called into existence since that date. The celebrated work of Bunsen and Kirchhoff was not published till 1859. Neither can I refrain from reminding you that the coal-tar colour industry, with which I have been to a small extent connected, was started into activity by Perkin's discovery of mauve in 1856; the reaction of this industry on the development of organic chemistry is now too well known to require further mention. In that direction also which brings chemistry into relationship with biology, the progress has been so great that it is not going beyond the fact to state that a new science has been created. Pasteur began his studies on fermentation in 1857, and out of that work has arisen the science of bacteriology, with its multifarious and far-reaching consequences. As this chapter of chemical history forms the subject of one of the evening discourses at the present meeting, it is unnecessary to dwell further upon it now. One other generalisation may be chronicled among the great developments achieved since 1851. I refer to the periodic law connecting the atomic weights of the chemical elements with their physical and chemical properties. Attempts to establish numerical relationships in the case of isolated groups of elements had been made by Döbereiner in 1817, by Gmelin in 1826, and again by Döbereiner in 1829. The triad system of grouping was further developed by Dumas in 1851. I am informed by Dr. Gladstone that at the last Ipswich meeting Dumas' speculations in this direction excited much interest. All the later steps of importance have, however, been made since that time, viz., by de Chancourtois in 1862, the "law of octaves" by Newlands in 1864, the periodic law by Mendeleeff, and almost contemporaneously by Lothar Meyer, in 1869.

I have been tempted into giving this necessarily fragmentary and possibly tedious historical sketch because it is approaching half a century since the British Association visited this town, and the opportunity seemed favourable for going through that process which in commercial affairs is called "taking stock." The result speaks for itself. Our students of the present time who are nourished intellectually by these doctrines should be made to realise how rapid has been their development. The pioneers of our science on whose shoulders we stand—and many of whom are happily still among us—will derive satisfaction from the retrospect, and will admit that their labours have borne goodly fruit. It is not, however, simply for the purpose of recording this enormous progress that I have ventured to assume the office of stock-taker. The year 1851 may be regarded as occurring towards the close of one epoch and the dawn of a new era in chemical history. Consider broadly the state of organic chemistry at that time. There is no occasion for going into detail, even if time admitted, because our literature has recently been enriched by the concise and excellent historical works of Schorlemmer, and of Ernst von Meyer. It will suffice to mention that the work and writings of Liebig, Berzelius, Wöhler, Dumas, Gay-Lussac, Bunsen, and others, had given us the leading ideas of isomerism, substitution, compound radicals, and types. Wurtz and Hofmann had just discovered the organic ammonias; Williamson that same year made known his celebrated work on the ethers; and Gerhardt discovered the acid anhydrides a year later. The newer theory of types was undergoing development by Gerhardt and his followers; the mature results were published in the fourth volume of the "Traité de Chimie" in 1856. In this country the theory was much advanced by the writings of Odling and Williamson.

SUBSEQUENT DEVELOPMENT OF CHEMISTRY ALONG TWO LINES.

The new era which was dawning upon us in 1851 was that of structural or constitutional chemistry, based on the doctrine of the valency of the atoms. It is well known that this conception was broached by Frankland in 1852, as the result of his investigations on the organo-metallic

compounds. But it was not till 1858 that Kekulé, who had previously done much to develop the theory of types, and Couper, almost simultaneously, recognised the quadrivalent character of carbon. To attempt to give anything approaching an adequate notion of the subsequent influence of this idea on the progress of organic chemistry would be tantamount to reviewing the present condition of that subject. I imagine that no conception more prolific of results has ever been introduced into any department of science. If we glance back along the stream it will be seen that shortly after the last meeting here the course of discovery began to concentrate itself into two channels. In one we now find the results of the confluent labours of those who have regarded our science from its physical side. In the other channel is flowing the tide of discovery arising from the valency doctrine and its extension to the structure of chemical molecules. The two channels are at present fairly parallel and not far apart; an occasional explorer endeavours now and again to make a cross-cut so as to put the streams into communication. The currents in both are running very rapidly, and the worker who has embarked on one or the other finds himself hurried along at such a pace that there is hardly breathing time to step ashore and see what his neighbours are doing. It speaks well for the fertility of the conception of valency that the current in this channel is flowing with unabated vigour, although its catchment area—to pursue the metaphor—is by no means so extensive as that of the neighbouring stream.

The modern tendency to specialisation, which is a necessity arising from the large number of workers and the rapid multiplication of results, is apparently in the two directions indicated. We have one class of workers dealing with the physics of matter in relation to general chemical properties, and another class of investigators concerning themselves with the special properties of individual compounds and classes of compounds—with atomic idiosyncracies. The workers of one class are differentiating while their colleagues are integrating. It would be nothing less than unscientific to institute a comparison between the relative merits of the two methods; both are necessary for the development of our science. All methods of attacking the unknown are equally welcomed. In some cases physical methods are available; in other cases purely chemical methods have alone been found of use. There is no antagonism, but co-operation. If the results of the two methods are sometimes at variance it is simply because we have not known how to interpret them. The physical chemist has adopted the results of the application of chemical methods of determining "constitution," and is endeavouring to furnish us with new weapons for attacking this same problem. The chemist who is seeking to unravel the architecture of molecules is dependent at the outset upon physical methods of determining the relative weights of his molecules. The worker who is bringing about new atomic groupings is furnishing material for the further development of generalisations from which new methods applicable to the problem of chemical structure may again be evolved. The physical chemist sometimes, from the broadness of his view, is apt to overlook or to minimise the importance of chemical individuality. On the other hand, the chemist who is studying the numberless potentialities of combination resident in the atoms, and who has grasped to the full extent their marvellous individualities, is equally liable to forget that there are connecting relationships as well as specific differences in the properties of elements and compounds. These are but the mental traits—the unconscious bias engendered by the necessary specialisation of work to which I have referred, and which is observable in every department of scientific labour.

THE PRESENT STATE OF STRUCTURAL CHEMISTRY.

The success attending the application of the doctrine of valency to the compounds of carbon has helped its

extension to all compounds formed by other elements, and the student of the present day is taught to use structural formulæ as the ABC of his science. It is, I think, generally recognised among chemists that this doctrine in its present state is empirical, but it does not appear to me that this point is sufficiently insisted upon in chemical teaching. I do not mean to assert that for the last thirty years chemists have been pursuing a phantom; neither do I think that we should be justified in applying to this doctrine the words applied to its forerunner, the "types" of Gerhardt, by Lothar Meyer, who says that these "have rendered great service in the development of the science, but they can only be regarded as a part of the scaffolding which was removed when the erection of the system of organic chemistry had made sufficient progress to be able to dispense with it" ("Modern Theories of Chemistry," p. 194). It appears to me, on the contrary, that there is a physical reality underlying the conception of valency, if for no other reason because of the conformability of this property of the atoms to the periodic law. But the doctrine as it stands is empirical, in so far that it is only representative and not explanatory. Frankland and Kekulé have given us a great truth, but its very success is now making it more and more obvious that it is a truth which is pressing for further development from the physical side. If we are asked why CO exists, and why CH₄ and CCl₄ do not, together with innumerable similar questions which the inquisitive mind will raise, we get no light from this doctrine. If any over-sanguine disciple goes so far as to assert that all the possible compounds of the elements indicated by their valency are capable of existence, and will sooner or later be prepared, he will, I imagine, find himself rapidly travelling away from the region of fact.

There is something to be reckoned with besides valency. The one great desideratum of modern chemistry is unquestionably a physical or mechanical interpretation of the combining capacities of the atoms. Attempts at the construction of such theories have been made, but thus far only in a tentative way, and these views cannot be said to have yet come within the domain of practical chemical politics. I have in mind, among other suggestions, the dynamical theory of van't Hoff, published in 1882 ("Ansichten über die organische Chemie"), the theory of electric charges on the atoms broached by Johnstone Stoney in 1874, and so ably advocated by the late Professor v. Helmholtz in his Faraday lecture in 1881, and the electric polar theory of Victor Meyer and Riecke, published in 1888 ("Einige Bemerkungen über den Kohlenstoffatom und die Valenz," *Ber.*, xxi., 946, 1620).

Pending the rationalisation of the doctrine of valency, its promulgation must continue in its present form. Its services in the construction of rational formulæ, especially within the limits of isomerism, have been incalculable. It is the ladder by which we have climbed to the present brilliant achievements in chemical synthesis, and we are not in a position to perform the ungracious task of kicking it away. In recalling attention to its weaknesses I am only putting myself in the position of the physician who diagnoses his patient's case with the ulterior object of getting him strengthened. There can be no doubt that renewed vitality has been given to the doctrine by the conceptions of tautomerism and desmotropy, formulated by Conrad Laar in 1885, and by Paul Jacobson in 1887. The importance of these ideas is becoming more evident with the advancement of chemical discovery. Any attempt to break down the rigidly statical conception of our structural formulæ appears to me to be a step in the right direction. Then, again, I will remind you of the prolific development of the doctrine in the hands of Le Bel and van't Hoff by the introduction of the stereochemical hypothesis in 1874—unquestionably the greatest advance in structural chemistry since the recognition of the quadrivalent character of the carbon atom. If evidence be required that there is a physical reality underlying the conception of valency, we need only point to the close

accordance of this notion of the asymmetric carbon atom with the facts of so-called "physical isomerism" and the splendid results that have followed from its introduction into our science, especially in the field of the carbohydrates, through the investigations of Emil Fischer and his pupils. In other directions the stereochemical hypothesis has proved to be a most suggestive guide. It was applied by Professor v. Baeyer in 1885 (*Ber.*, xviii., 2277) to explain the conditions of stability or instability of certain atomic groupings, such as the explosiveness of polyacetylene compounds and the stability of penta- and hexa-cyclic systems. Again, in 1888 this eminent chemist showed its fertility in a series of brilliant researches upon benzene derivatives (*Ann.*, cxxvii., 158, and subsequent papers). Nor can I omit to mention the great impetus given in this field by the classical work of Wislicenus, who in 1887 applied the hypothesis to unsaturated compounds and to cyclic systems with remarkable success ("Ueber die räumliche Anordnung der Atome in organischen Molekülen," &c.). Quite recently Viçor Meyer and J. Sudborough have shown that the ability of certain derivatives of benzoic and naphthoic acids to form ethers is governed by stereochemical considerations (*Ber.*, xxvii., 510, 1580, 3146, and xxviii., 182, 1254). But I must avoid the temptation to enlarge upon this theme, because the whole subject has been recently brought together by C. A. Bischoff in his "Handbuch der Stereochemie" (Frankfurt, 1893-94), a work to which all who are interested in the subject will naturally turn for reference.

While the present advanced state of structural chemistry may thus be looked upon as the outcome of the conceptions of Frankland and Kekulé, it may be well to bear in mind that the idea of structure is not necessarily bound up with the hypothesis of valency in its present form. Indeed, some advance had been made in representing "constitution," especially by Kolbe, before the formal introduction of this hypothesis. The two ideas have grown up together, but the experimental evidence that in any molecule the atoms are grouped together in a particular way is really independent of any theory of valency. It is only after this evidence has been acquired, either by analysis or synthesis, that we proceed to apply the hypothesis in building up the structural formula. It is of course legitimate to assume the truth of the hypothesis, and to endeavour by its use to convert an empirical into a rational formula; but this method generally gives us a choice of formulæ from which the true one can only be selected by further experimental investigation. Even within the narrower limits of isomerism it is by no means certain that all the modifications of a compound indicated by hypothesis are actually capable of existence. There is, for example, evidence that some of the "position isomerides" among the derivatives of mono- and polycyclic compounds are too unstable to exist—a fact which in itself is sufficient to indicate the necessity for a revision and extension of our notions of valency. Thus, by way of illustration, there is nothing in the hypothesis to indicate why orthoquinones of the benzene series should not be capable of existence; yet it is a fact that in spite of all efforts such compounds have never been obtained. The conditions essential for the existence of these compounds appear to be that the hydrogen of the benzene ring should be replaced by acid substituents such as oxygen, hydroxyl, chlorine, or bromine. Under these circumstances, as Zincke has shown (*Ber.*, xx., 1776), tetrachlor and tetrabrom-orthobenzoquinone are stable compounds. So also the interesting researches of Nietzki have proved that in such a compound as rhodizonic acid (*Ber.*, xix., 308, and xxiii., 3136) orthoquinone oxygen atoms are present. But there is nothing in the doctrine of valency which leads us to suspect that these orthoquinone derivatives can exist while their parent compound resists all attempts at isolation. I am aware that it is dangerous to argue from negative evidence, and it would be rash to assert that these orthoquinones will never be obtained. But even in the present state of knowledge it

may be distinctly affirmed that the methods which readily furnish an orthoquinone of naphthalene completely fail in the case of benzene, and it is just on such points as this that the inadequacy of the hypothesis becomes apparent. In other words, the doctrine fails in the fundamental requirement of a scientific theory; in its present form it gives us no power of prevision—it hints at possibilities of atomic groupings, but it does not tell us *a priori* which of these groupings are likely to be stable and which unstable. I am not without hope that the next great advance in the required direction may yet come from the stereochemical extension of the hypothesis, although the attempts which have hitherto been made to supply its deficiencies cannot but be regarded as more or less tentative.

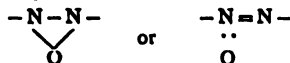
THE NEW THEORY OF ABSTRACT TYPES.

I will venture, in the next place, to direct attention to a modern development of structural chemistry which will help to illustrate still further some of the points raised. For many years we have been in the habit of abstracting from our structural formulæ certain ideal complexes of atoms which we consider to represent the nucleus or type from which the compound of known constitution is derived. In other words the hypothesis of valency which was developed originally from Gerhard's types is now leading us back to another theory of types based upon a more intimate knowledge of atomic grouping within the molecule. In some cases these types have been shown to be capable of existence; in others they are still ideal. Used in this way the doctrine of valency is most suggestive, but at the same time its lack of prevision is constantly forcing itself upon the attention of chemical investigators. The parent compound has sometimes been known before its derivatives, as in the case of ammonia, which was known long before the organic amines and amides. In other instances the derivatives were obtained before the type was isolated, as in the case of the hydrazines, which were characterised by Emil Fischer in 1875, and the hydrazo compounds, which have been known since 1863, while hydrazine itself was first obtained by Curtius in 1887. Phenylazimide was discovered by Griess in 1864, and many representatives of this group have been since prepared; but the parent compound, hydrazoic acid, was only isolated by Curtius in 1890. Derivatives of triazole and tetrazole were obtained by Bladin in 1885; the types were isolated by this chemist and by Andreocci in 1892. Pyrazole derivatives were prepared by Knorr in 1883; pyrazole itself was not isolated till 1889, by Buchner. Alkyl nitramides were discovered by Franchimont and Klobbie many years before the typical compound, nitramide, NO_2NH_2 , which was isolated last year by Thiele and Lachman (*Ber.*, xxvii., 1909). Examples might be multiplied to a formidable extent, but enough have been given to illustrate the principle of the erection of types, which were at first imaginary, but which have since become real. The utility of the hypothesis is undeniable in these cases, and we are justified in pushing it to its extreme limits. But no chemist, even if endowed with prophetic instinct, could have certainly foretold six years ago that the type of Griess's "triazobenzene" would be capable of free existence, and still less that when obtained it would prove to be a strong acid. The fact, established by Car-

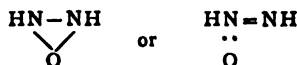
tus, that the group $\text{N} \begin{matrix} \diagup \\ \diagdown \end{matrix} \text{N}$ - functions in chemical molecules like the atom of chlorine is certainly among the most striking of recent discoveries. Only last year the list of nitrogen compounds was enriched by the addition of $\text{CO}(\text{N}_3)_2$, the nitrogen analogue of phosgene (Curtius, *Ber.*, xxvii., 2684).

These illustrations, drawn from the compounds of nitrogen, will serve to bring out the wonderful development which our knowledge of the chemistry of this element has undergone within the last few years. I might be tempted here into a digression on the general bearing of

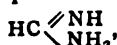
the very striking fact that an element comparatively inactive in the free state should be so remarkably active in combination, but I must keep to the main topic, as by means of these compounds it is possible to illustrate still further both the strength and the weakness of our modern conceptions of chemical structure. Consider some of the undiscovered compounds which are foreshadowed by the process of ideal abstraction of types. The azoxy-compounds contain the complex



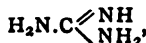
The types would be—



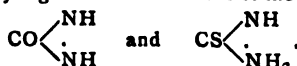
The first of these formulæ represents the unknown dihydro-nitrous oxide. The azo-compounds are derivatives of the hypothetical diimide HN:NH . An attempt to prepare this compound from azodicarbonic acid (Thiele, *Ann.*, cclxxi., 130) resulted in the formation of hydrazine. The diethyl-derivative may have been obtained by Harries (*Ber.*, xxvii., 2276), but this is doubtful. It is at present inexplicable why compounds in which the group $\cdot\text{N:N}\cdot$ is in combination with aromatic radicles should be so remarkably stable, while the parent compound appears to be incapable of existence. The addition of two atoms of hydrogen converts this type again into a stable compound. There is nothing in the structural formulæ to indicate these facts. The amidines are stable compounds, and the so called "anhydro-bases," or imidazoles, are remarkably stable; the parent compound—



has not been obtained, while its amido-derivative—

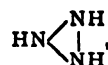


is the well-known substance, guanidine. The isodiazocompounds recently discovered by Schraube and Schmidt and by Bamberger (*Ber.*, xxvii., 514, 679, &c.) are possibly derivatives of the hypothetical substance O:N.NH_2 , which might be named nitrosamide. Why this compound should not exist as well as nitramide is another question raised by the principle of abstract types. The carbazines were formerly regarded as derivatives of the compounds—



(Fischer, *Ann.*, ccxii., 326; Freund and Goldsmith, *Ber.*, xxi., 2456). Although this structure has now been disproved the possible existence of the types has been suggested. Carbazine and thiocarbazine differ from urea and thiocarbamide only by two atoms of hydrogen. These types have not been isolated; if they are incapable of existence the current views of molecular structure give no suggestion of a reason. The diazoamides are derivatives of the hypothetical $\text{H}_2\text{N.NH.NH}_2$ or HN:N.NH_2 , compounds which Curtius speaks of as the propane and propylene of the nitrogen series. The latter complex was at one time thought to exist in diazohippuramide (*Ber.*, xxiv., 3342; this has since been shown to be hippurazide, i. e., a derivative of N_3H (*Ber.*, xxvii., 779), and a biacydyl derivative of the former type has also been obtained (*Ber.*, 3344). Both these types await isolation if they are capable of existence. I may add that several attempts to convert diazoamides into dihydro-derivatives by mild alkaline reduction have led me to doubt whether this nitrogen chain can exist in combination with hydrocarbon radicles. The bisdiazooamides of H. v. Pechmann and Frobenius (*Ber.*, xxvii., 898) are derivatives of the 5-atom chain $\text{H}_2\text{N.NH.NH.NH.NH}_2$ or HN:N.NH.N:NH , a type which hardly seems likely to be of sufficient stability to exist. The tetrazones of Emil Fischer have for their type

the 4-atom chain $\text{H}_2\text{N.N:N.NH}_2$ or $\text{H}_2\text{N.NH.NH.NH}_2$, of which the free existence is equally problematical, although a derivative containing the chain —N:N.NH.NH— has been obtained by Curtius (*Ber.*, xxvi., 1263). Hydrazoic acid may be regarded as a derivative of triimide—



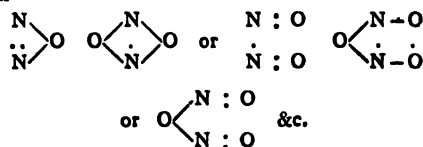
but this type appears to be also incapable of isolation (Curtius, *Ber.*, xxvi., 407). The hydrazidines or formazyls of Pinner (*Ber.*, xvii., 182) and of H. v. Pechmann (*Ber.*, xxv., 3175) have for their parent compound the hypothetical substance $\text{H}_2\text{N.N:CH.N:NH}$. In 1888 Limpricht described certain azo-compounds (*Ber.*, xxi., 3422) which, if possessing the structure assigned by that author, must be regarded as derivatives of diamidotetrimide—



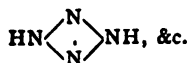
Both these types are at present imaginary; whether it is possible for cyclic nitrogen systems to exist we have no means of knowing—all that can be said is that they have never yet been obtained. It is possible, as I pointed out in 1890 at the Leeds meeting of the British Association, that mixed diazoamides may be derivatives of such a 4-atom ring.

Any chemist who has followed the later developments of the chemistry of nitrogen could supply numerous other instances of undiscovered types. A chapter on the unknown compounds of this element would furnish quite an exciting addition to many of those books which are turned out at the present time in such profusion to meet the requirements of this or that examining body. I have selected my examples from these compounds simply because I can claim some of them as personal acquaintances. It would be easy to make use of carbon compounds for the same purpose, but it is unnecessary to multiply details. It has frequently happened in the history of science that a well-considered statement of the shortcomings of a theory has led to its much-desired extension. This is my hope in venturing to point out one of the chief deficiencies in the structural chemistry of the present time. I am afraid that I have handled the case badly, but I am bound to confess that I am influenced by the same feelings as those which prevent us from judging an old and well-tried friend too severely.

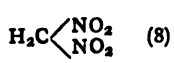
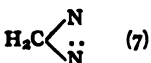
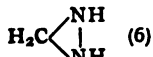
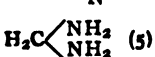
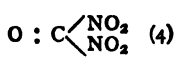
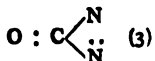
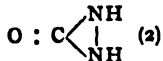
The theory of types to which we have reverted as the outcome of the study of molecular structure is capable of almost indefinite extension if, as there is good reason for doing, we replace atoms or groups by their valency analogues in the way of other atoms or groups of atoms. The facts that in cyclic systems N can replace CH (benzene and pyridine), that O, S, and NH are analogues in furfuran, thiophene, and pyrrole, are among the most familiar examples. The remarkable iodo- and iodoso-compounds recently discovered by Victor Meyer and his colleagues are the first known instances in which the trivalent atom of iodine has been shown to be the valency analogue of nitrogen in organic combination. Pushing this principle to the extreme we get further suggestions for new groupings, but, as before, no certainty of prevision. Thus, if nitrogen formed the oxide N_2O_2 the series might be written—



Of course these formulæ are more or less conjectural, being based on valency only. But since nitrous oxide is the analogue of hydrazoic acid, they hint at the possibility of such compounds as—



If a student produced a set of formulæ corresponding to the above, in which NH had been substituted for O, and asked whether they did not indicate the existence of a whole series of unknown hydrogen compounds of nitrogen, we should probably tell him that his notions of chemical structure had run wild. At the same time I am bound to admit that it would be very difficult, if not impossible, to furnish him with satisfactory reasons for believing that such groupings are improbable. Compare again the series—



The first is urea; the second, third, fourth, fifth (methylene diamine), and sixth are unknown; the seventh is the remarkably interesting diazomethane discovered last year by H. v. Pechmann (*Ber.*, xxvii., 1888). The last compound, dinitromethane, is known in the form of its salts, but appears to be incapable of existence in the free state. There is nothing expressed or implied in the existing theory of chemical structure to explain why dinitromethane is unstable while trinitromethane is stable, and mono- and tetranitromethane so stable as to admit of being distilled without decomposition. Chemists will form their own views as to the possibility or impossibility of such a series as this being completed. Whether there would be a concordance of opinion I will not venture to say: but any chemist who expressed either belief or disbelief with regard to any special member would, I imagine, have great difficulty in giving a scientific reason for the faith which is in him. At the most he would have only the very unsafe guide of analogy to fall back upon. Perhaps by the time the British Association holds its next meeting at Ipswich it will have become possible to prove that one particular configuration of certain atoms is possible and another configuration impossible. Then will have been achieved that great advance for which we are waiting—the reunion of the two streams into which our science began to diverge shortly after the last Ipswich meeting.

The present position of structural chemistry may be summed up in the statement that we have gained an enormous insight into the anatomy of molecules, while our knowledge of their physiology is as yet in a rudimentary condition. In the course of the foregoing remarks I have endeavoured to indicate the direction in which our theoretical conceptions are most urgently pressing for extension. It is, perhaps, as yet premature to pronounce an opinion as to whether the next development is to be looked for from the stereochemical side; but it is not going too far to express once again the hope that the geometrical representation of valency will give us a deeper insight into the conditions which determine the stability of atomic configurations. The speculations of A. v. Baeyer, Wislicenus, Victor Meyer, Wunderlich, Bischoff, and others have certainly turned the attention of chemists towards a quarter from which a new light may eventually dawn.

THE PROGRESS OF SYNTHETICAL CHEMISTRY.

If, in my earnest desire to see the foundations of structural chemistry made more secure, I may have unwittingly given rise to the impression that I am depreciating its

services as a scientific weapon, let me at once hasten to make amends by directing attention to the greatest of its triumphs, the synthesis of natural products, i.e., of compounds which are known to be produced by the vital processes of animals and plants.

Having been unable to find any recent list of the natural compounds which have been synthesised, I have compiled a set of tables which will, I hope, see the light at no very distant period. According to this census we have now realised about 180 such syntheses. The products of Bacteria have been included in the list because these compounds are the results of vital activity in the same sense that alcohol is a product of the vital activity of the yeast plant. On the other hand, the various uro-compounds resulting from the transformation in the animal economy of definite chemical substances administered for experimental purposes have been excluded, because I am confining my attention to natural products. Of course, the importance of tracing the action of the living organism on compounds of known constitution from the physiological point of view cannot be over-estimated. Such experiments will, without doubt, in time shed much light on the working of the vital laboratory.

The history of chemical synthesis has been so thoroughly dealt with from time to time that I should not have ventured to obtrude any further notice of this subject upon your patience were it not for a certain point which appeared to me of sufficient interest to merit re-consideration. It is generally stated that the formation of urea from ammonium cyanate by Wöhler in 1828 was the first synthesis of an organic compound. There can be no doubt that this discovery, which attracted much attention at the time, gave a serious blow to the current conceptions of organic chemistry, because urea was so obviously a product of the living animal. It will be found, however, that about the same time Henry Hennell, of Apothecaries' Hall, had really effected the synthesis of alcohol—that is to say, had synthesised this compound in the same sense that Wöhler had synthesised urea. The history is soon told. In 1826 Hennell (through Brande) communicated a paper to the Royal Society which appears in the *Philosophical Transactions* for that year ("On the Mutual Action of Sulphuric Acid and Alcohol, with Observations on the Composition and Properties of the Resulting Compound," *Phil. Trans.*, 1826, p. 240). In studying the compounds produced by the action of sulphuric acid on alcohol, and known as "oil of wine," he obtained sulphovinic acid, which had long been known, and gave fairly good analyses of this acid and of some of its salts, while expressing in the same paper very clear notions as to its chemical nature. Having satisfied himself that sulphovinic acid is a product of the action in question, he then proceeded to examine some sulphuric acid which had absorbed eighty times its volume of olefiant gas, and which had been placed at his disposal for this purpose by Michael Faraday. From this he also isolated sulphovinic acid. In another paper, communicated to the Royal Society in 1828 ("On the Mutual Action of Sulphuric Acid and Alcohol, and on the Nature of the Process by which Ether is formed," *Phil. Trans.*, 1828, p. 365), he proves quantitatively that when sulphovinic acid is distilled with sulphuric acid and water the whole of the alcohol and sulphuric acid which united to form the sulphovinic acid are recovered. In the same paper he shows that he had very clear views as to the process of etherification. Hennell's work appears to have been somewhat dimmed by the brilliancy of his contemporaries who were labouring in the same field; but it is not too much to claim for him, after the lapse of nearly seventy years, the position of one of the pioneers of chemical synthesis. Of course, in his time the synthesis was not complete, because he did not start from inorganic materials. The olefiant gas used by Faraday had been obtained from coal-gas or oil-gas. Moreover, in 1826-1828 alcohol was not generally regarded as a product of vital activity, and this is, no doubt, the reason why the discovery failed to

produce the same excitement as the formation of urea. But the synthesis of alcohol from ethylene had, nevertheless, been accomplished, and this hydrocarbon occupied at that time precisely the same position as ammonium cyanate. The latter salt had not then been synthesised from inorganic materials, and the formation of urea, as Schorlemmer points out ("The Rise and Development of Organic Chemistry," p. 195), was also not a complete synthesis. The reputation of Wöhler, the illustrious friend and colleague of the more illustrious Liebig, will lose not a fraction of its brilliancy by the raising of this historical question. Science recognises no distinction of nationality, and the future historian of synthetical chemistry will not begrudge the small niche in the temple of Fame to which Hennell is entitled.

Like many other great discoveries in science, the artificial formation of natural products began, as in the case of alcohol and urea, with observations arising from experiments not primarily directed to this end. It was not till the theory of chemical structure had risen to the rank of a scientific guide that the more complicated syntheses were rendered possible by more exact methods. We justly credit structural chemistry with these triumphant achievements. In arriving at such results any defects in the theory of structure are put out of consideration, because—and this point must never be lost sight of—all doubt as to the possibility of this or that atomic grouping being stable is set aside at the outset by the actual occurrence of the compound in nature. The investigator starts with the best of all assurances. From the time of Wöhler and Hennell the course of discovery in this field has gone steadily on. The announcement of a new synthesis has ceased to produce that excitement which it did in the early days when the so-called "organic" compounds were regarded as products of special vital force. The interest among the uninitiated now rises in proportion to the technical value of the compound. The present list of 180 odd synthetical products comprises, among the latest discoveries, gentisin, the colouring-matter of the gentian root (*Gentiana lutea*), which has been prepared by Kostanecki and Tambor, and caffeine, synthesised by Emil Fischer and Lorenz Ach, starting from dimethylurea and malonic acid.

I have allowed myself no time for those prophetic flights of the imagination which writers on this subject generally indulge in. When we know more about the structure of highly complex molecules, such as starch and albumen, we shall probably be able to synthesise these compounds. It seems to me more important just at present to come to an understanding as to what is meant by an organic synthesis. There appears to be an impression among many chemists that a synthesis is only effected when a compound is built up from simpler molecules. If the simpler molecules can be formed directly from their elements, then the synthesis is considered to be complete. Thus urea is a complete synthetical product, because we can make hydrogen cyanide from its elements: from this we can prepare a cyanate, and finally urea. In dictionaries and text-books we find synthetical processes generally separated from modes of formation, and the latter in their turn kept distinct from methods of preparation. The distinction between formation and preparation is obviously a good one, because the latter has a practical significance for the investigator. But the experience gained in drawing up the tables of synthesised compounds, to which I have referred, has resulted in the conclusion that the terms "synthesis" and "mode of formation" have been either unnecessarily confused or kept distinct without sufficient reason, and that it is impossible now to draw a hard-and-fast line between them. Some recent writers, such, for example, as Dr. Karl Elbs, in his admirable work on this subject ("Die Synthetischen Darstellungsmethoden der Kohlenstoffverbindungen," Leipzig, 1889), have expanded the meaning of the word synthesis so as to comprise generally the building up of organic molecules by the combination of carbon with carbon, without

reference to the circumstance whether the compound occurs as a natural product or not. But although this definition is sufficiently wide to cover the whole field of the production of carbon compounds from less complex molecules, it is in some respects too restricted, because it excludes such well known cases as the formation of hydrogen cyanide from its elements, or of urea from ammonium cyanate. I should not consider the discussion of a mere question of terminology of sufficient importance to occupy the attention of this Section were it not for a matter of principle, and that a principle of the very greatest importance, which I believe to be associated with a clear conception of chemical synthesis. The great interest of all work in this field arises from our being able, by laboratory processes, to obtain compounds which are also manufactured in Nature's laboratory—the living organism. It is in this direction that our science encroaches upon biology through physiology. Now, if we confine the notion of synthesis to the building up of molecules from simpler molecules or from atoms, we exclude one of Nature's methods of producing many of these very compounds which we claim to have synthesised. There can be no manner of doubt that a large proportion, if not a majority, of the natural products which have been prepared artificially are not synthesised by the animal or plant in the sense of building up at all. They are the results of the breaking down—of the degradation—of complex molecules into simpler ones. I urge, therefore, that if in the laboratory we can arrive at one of these products by decomposing a more complex molecule by means of suitable reagents, we have a perfect right to call this a synthesis, provided always that the more complex molecule, which gives us our compound, can be in its turn synthesised, by no matter how many steps, from its constituent atoms. Thus, oxalic acid has been directly synthesised from carbon dioxide by Kolbe and Drechsel by passing this gas over potassium or sodium amalgam heated to 360°. Whether the plant makes oxalic acid directly out of carbon dioxide we cannot at present state; if it does it certainly does not employ Kolbe and Drechsel's process. On the other hand, this acid may, for all that is known, exist in the plant as a product of degradation. Many more complex acids, such as citric and tartaric, break down into oxalic acid when fused with potash. Both citric and tartaric acids can now be completely synthesised; therefore the formation of oxalic acid from these by potash fusion is a true synthesis.

The illustration given will make clear the point which I am urging. The distinction between a synthesis and a mode of formation vanishes when we can obtain a compound by the breaking down of a more complex molecule in all those cases where the latter can be completely built up. If we do not expand the meaning of synthesis so as to comprise such cases we are simply shutting the door in Nature's face. It must be borne in mind that the actual yield of the compound furnished by the laboratory process does not come into consideration, because it may be generally asserted that in most cases the artificial processes are not the same as those which go on in the animal or plant. The information of real value to the physiologist which these syntheses give is the suggestion that such or such a compound may possibly result from the degradation of this or that antecedent compound, and not from a process of building up from simpler molecules.

THE BEARING OF CHEMICAL SYNTHESIS ON VITAL CHEMISTRY.

With these views—the outcome of structural chemistry—the chemist and physiologist may join hands and move fearlessly onwards towards the great mystery of vital chemistry. In considering the results of organic synthesis two questions always arise, as it were spontaneously: How does Nature produce these complicated molecules without the use of strong reagents and at ordinary temperatures? What bearing have our laboratory achieve-

ments on the mechanism of vitality? The light shed upon these questions by experimental investigation has as yet flickered only in fitful gleams. We are but dwellers in the outer gates, waiting for the guide who is to show us the bearing of modern research on the great problem which confronts alike the physicist, the chemist, and the biologist. The chemical processes that go on in the living organism are complex to an extent that is difficult to realise. Of the various compounds of animal or vegetable origin that have been produced synthetically, some are of the nature of waste products, resulting from metabolic degradation; others are the result of zynolytic action within the organism; and others, again, are secondary products arising from the action of associated Bacteria, the relationship between the Bacteria and their host being as yet imperfectly understood. The answer to the question how Nature produces complicated organic molecules will be much facilitated when the physiologist, by experiment and observation, shall have made possible a sound classification of these synthetical products based on their mode of origination in the organism.

The enlargement of the definition of organic synthesis which I have advocated has been rendered necessary by the consideration of certain questions which have arisen in connection with the present condition of chemical discovery in this field. What evidence is there that any one of the 180 compounds which have been prepared artificially is produced in the organism by a direct process of building up? Is not the opposite view quite as probable? May they not, from the simplest to the most complex, be products of the degradation of still more complex molecules? I venture to suggest—not without some temerity, lest our colleagues of Sections I and K should treat me as an intruder—that this view should be given a fair trial. I am aware that the opposite view, especially as regards plant assimilation, has long been held, and especially since 1870, when v. Baeyer advanced his celebrated theory of the formic aldehyd origin of carbohydrates. It is but natural to consider that the formation of a complex molecule is the result of a building-up process. It must be remembered, however, that in the living organism there is always present a compound or mixture, or whatever we like to call it, of a highly complex proteid nature, which, although at present indefinite from the purely chemical point of view, is the essence of the vitality. Of course I refer to what biologists have called protoplasm. Moreover, it is perhaps necessary to state what is really nothing more than a truism, viz., that protoplasm is present in and forms a part of the organism from the very beginning of its existence—from the germ to the adult, and onwards to the end of life. Any special chemical properties pertaining to protoplasm are inseparable from the animal or plant until that period arrives which Kekulé has hinted at when we shall be able to "build up the formative elements of living organisms" in the laboratory (*Nature*, xviii., 212). But here I am afraid I am allowing the imagination to take a flight which I told you a few minutes ago that time would not admit of.

The view that requires pushing forward into a more prominent position than it has hitherto occupied is that all the chemical transformations in the organism—at any rate all the primary changes—are made possible only by the antecedent combination of the substances concerned with living protoplasmic materials. The carbon dioxide, water, &c., which the plant absorbs, must have formed a compound or compounds with the protoplasmic material of the chloroplasts before starch, or sugar, or cellulose can be prepared. There is, on this view, no such process as the direct combination of dead molecules to build up a complex substance. Everything must pass through the vital mill. The protoplasmic molecule is vastly more complex than any of the compounds which we have hitherto succeeded in synthesising. It might take up and form new and unstable compounds with carbon dioxide or formic aldehyd, or sugar, or anything else, and our present methods of investigation would fail to reveal the pro-

cess. If this previous combination and, so to speak, vitalisation of dead matter actually occurs, the appearance of starch as the first visible product of assimilation, as taught by Sachs, or the formation of a 12-carbon-atom sugar as the first carbohydrate, as shown by the recent researches of Horace Brown and G. H. Morris, is no longer matter for wonderment. The chemical equations given in physiological works are too purely chemical; the physiologists have, I am afraid, credited the chemists with too much knowledge—it would appear as though their intimate familiarity with vital processes had led them to undervalue the importance of their prime agent. In giving expression to these thoughts I cannot but feel that I am treating you to the strange spectacle of a chemist pleading from the physiologists for a little more vitality in the chemical functions of living organisms. The future development of vital chemistry rests, however, with the chemist and physiologist conjointly; the isolation, identification, and analysis of the products of vital activity, which has hitherto been the task of the chemist, is only the preliminary work of physiological chemistry leading up to chemical physiology.

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING AUGUST 31ST, 1895.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, September 10th, 1895.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Aug. 1st to Aug. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined two were recorded as "clear, but dull;" the remainder being clear, bright, and well filtered.

The rainfall in the Thames Valley during August has been close upon the average. The actual amount is 2.28 inches, and the twenty-five years' mean is 2.24, showing an excess of 0.04 inch. By far the greater part of the rain fell in the first part of the month, only 0.36 inch having fallen since the 14th.

The Thames-derived waters still maintain the high degree of purity we had to record in the reports for June and July. Compared with the waters in July, there is scarcely any analytical difference. Compared with the waters for the corresponding month last year, there is an appreciable diminution in some of the constituents, as seen by the following table.

Our bacteriological examinations of the unfiltered Thames waters and of the clear water drawn from the general wells of the Water Companies show that the microbial life in the river is diminishing, whilst the Com-

Comparison of the Averages of the Five Thames-derived Supplies for the Months of August, 1894 and 1895.

Common Salt. Per gall. Means.	Nitric Acid. Per gall. Means.	Hardness. Degrees. Means.	Oxygen. reqd. Per gall. Means.	Organic Carbon. Per gall. Means.	Organic Carbon. Per gall. Maxima.	Colour. Br'n: Blue. Means.
Aug., 1894	2°077	0°389	12°30	0°048	0°105	0°138
1895	1°994	0°740	13°09	0°039	0°093	0°108

panies' filters continue to work with efficiency. The unfiltered waters contained an average of 1720, and the clear filtered waters flowing into the pipes contained an average of 34 bacteria per c.c. These were all harmless river microbes.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

CORRESPONDENCE.

DISINFECTANTS.

To the Editor of the Chemical News.

SIR,—In your reviewer's notice of my book on "Disinfectants" he adds to the following quotation from p. 11 the words which I have italicised:—"A large number of processes have endeavoured to recover the phosphate of sewage by using the sludge as a fertiliser, but they have all met with little commercial success;" and then proceeds to say, this statement "we must pronounce as utterly mistaken." His own additional words are those which have led him to express this opinion, as the context shows the phosphate referred to is not the phosphate of sewage, but the phosphate of animal charcoal, the whole of this section being devoted to remarks on the use of this material for purifying and deodorant purposes.—I am, &c.,

SAMUEL RIDEAL.

Chemical Laboratory,
28, Victoria St., Westminster, S.W.,
September 2, 1895.

MISCELLANEOUS.

British Association for the Advancement of Science.—The following are the names of the Officers and Committee of Section B (Chemical Science) at the Ipswich Meeting of the British Association:—

President—Prof. R. Meldola, F.R.S., Foreign Sec. C.S.
Vice-Presidents—Prof. P. P. Bedson, D.Sc.; Prof. H. B. Dixon, M.A., F.R.S.; Prof. E. Frankland, D.C.L., F.R.S.; Dr. J. H. Gladstone, Ph.D., F.R.S.; Prof. Ira Remsen, Ph.D.; Sir H. E. Roscoe, D.C.L., F.R.S.

Secretaries—E. Herbert Fison, C. A. Kohn, Arthur Harden (Recorder), J. W. Rodger.

Committee—Prof. H. E. Armstrong, F.R.S.; R. N. Atkinson; J. Carter Bell; C. H. Bothamley; Prof. J. Campbell Brown; Prof. F. Clowes; T. Fairley; A. E. Fletcher; C. J. Fowler; Prof. Franchimont; A. G. Vernon Harcourt, F.R.S., Pres. C.S.; Prof. Liveing, F.R.S.; Prof. H. McLeod, F.R.S.; H. Forster Morley; Manning Prentice; Lord Rayleigh, Sec. R.S.; A. Richardson; Prof. A. Smithells; J. Spiller; Prof. R. Warrington, F.R.S.; W. Marshall Watts; Prof. W. Carleton Williams; G. Young.

The Papers brought before the Section were as follows:—

President's Address.

Sir H. E. Roscoe and Arthur Harden—A New View of the Genesis of Dalton's Atomic Theory, derived from Original Manuscripts.

Dr. J. H. Gladstone—Report of the Committee on the Teaching of Science in Elementary Schools.

G. F. Fowler—The Action of Nitric Oxide on some Metallic Salts.

Prof. F. Clowes—The Respirability of Air in which a Candle Flame has Burnt until it is Extinguished.

D. J. P. Berridge—The Action of Light upon the Soluble Metallic Iodides in presence of Cellulose.

Dr. C. A. Kohn—Report of the Committee on Quantitative Analysis by means of Electrolysis.

Sir H. E. Roscoe—Report of the Committee Appointed to Prepare a New Series of Wave-length Tables of the Spectra of the Elements.

A Discussion was held in conjunction with Section K (Botany) on the Relation of Agriculture to Science. The Discussion was introduced by the following papers:—

Prof. R. Warrington—How Shall Agriculture best obtain Help from Science?

T. Hendrick—Agriculture and Science.

M. J. R. Dunstan—The Application of Science to Agriculture.

T. B. Wood—Work at the Experimental Plots in Norfolk and Suffolk.

Report of the Committee on the Preparation of Pure Haloids.

Report of the Committee on the Bibliography of Spectroscopy.

Dr. H. W. Vogel—Some Remarks on Orthochromatic Photography.

C. H. Bothamley—The Sensitising Action of Dyes on Gelatino-bromide Plates.

Report of the Committee on the Action of Light on Dyed Colours.

Dr. J. J. Sudborough—Some Stilbene Derivatives.

Dr. J. J. Sudborough—Note on the Constitution of Camphoric Acid.

Dr. M. Wildermann—Experimental Proof of Van't Hoff's Constant, of Dalton's Law, &c., for very Dilute Solutions.

H. J. H. Fenton—The Formation and Properties of a New Organic Acid.

Dr. M. Wildermann—On the Velocity of Reaction before perfect Equilibrium takes place.

C. F. Cross and C. Smith—The Chemical History of the Barley Plant.

Joint Sitting of Sections A and B:—

Lord Rayleigh, Sec. R.S.—On the Refraction and Viscosity of Argon and Helium.

Dr. J. H. Gladstone, F.R.S.—On Specific Refraction and the Periodic Law, with reference to Argon and other Elements.

A Discussion "On the Evidence to be gathered as to the Simple or Compound Character of a Gas, from the Constitution of its Spectrum." The Discussion was opened by Prof. A. Schuster, F.R.S. Lord Rayleigh, Sec. R.S., and Prof. Runge and others joined in the Discussion, and Dr. Johnstone Stoney, F.R.S., read a paper on "The Interpretation of Spectra."

The Chemical Laboratory of Wiesbaden.—In the Summer Term, 1895, there were fifty-four students on the books. Of these, thirty-four were from Germany, four from England, four from Norway, two from Austro-Hungary, two from Holland, two from Belgium, two from Australia; also one from each of the following countries—Switzerland, Italy, Russia, and United States of America. In place of Professor Borgmann, deceased in April, Dr. L. Grünhut has been nominated as teacher of chemical technology. Other changes in the teachers have not taken place. The assistants in the instruction laboratory were three in number, in the Versuchsstationen (private laboratories) twenty. The next Winter Term begins the 15th of October. The Versuchsstation has been appointed as one of the institutions where chemists can receive the practical instruction in the analysis of food necessary for

the admission to the examination for food analysts. During the last term, besides the scientific researches, a great number of analyses were undertaken in the different departments of the Laboratory and the Versuchsstation on behalf of manufacture, trade, mining, agriculture, and hygiene.

The People's Palace.—In the South Kensington Examinations last year, the Day School obtained 2 Honours First, 4 Honours Second; 56 Adv. First, 131 Adv. Second; 455 Elementary Passes. Evening Classes, 4 Hon. First, 7 Hon. Second; 23 Adv. First, 139 Adv. Second; 200 Elementary Passes in science subjects. In addition to these, 11 First, 68 Second, and 47 Elementary Passes were obtained by the Day School in Mathematics, and 3 First 26 Second, and 7 Passes by the Evening Class students. Among the latter are included 10 students who were successful in the Department Examination in Conic Sections and Differential and Integral Calculus. In Art, the Day School obtained 121 First and 138 Second, and the Evening Classes 2 Excellent, 104 First, and 135 Second. In the Evening Classes successes were likewise obtained in the City and Guilds Examination and in those of the University of London. Out of 50 London County Council Evening Exhibitions awarded to students from various polytechnics, 21 were obtained by those from the People's Palace. The chemical laboratory has been entirely re-fitted through the generosity of the Drapers' Company.

Charterhouse Science and Art Schools and Literary Institute.—The Winter Session will commence on Saturday, September 28th, under the Presidency of the Rev. Henry Swann, M.A. During the late Session upwards of 1200 students, mostly elementary teachers, availed themselves of the privileges offered by this Institution. Of this number, 682 presented themselves for examination, and were successful in obtaining a large number of certificates awarded by the Science and Art Department of South Kensington. Several students prepared for the Lond. B.Sc. (Int.) Examination. Instruction of a practical character is given in most of the sciences at a very nominal fee, whilst in Art at an equally low rate students, under the direction of competent instructors, can be advanced in their studies. Those who have leisure can, at a very moderate charge, attend the Day Classes in Art. Day Classes will be held to prepare candidates for Matriculation (Lond.), the Clerical, Medical (including Dental), and other Examinations. Students who aim at becoming proficient in Chemistry (Organic and Inorganic) have the opportunity of working in a well-fitted laboratory. Aspirants for university honours can, at a very small expense, be assisted in their studies. Classes for Matriculation, Microscopy, Latin, Greek, French, German, Shorthand, and Music are taught by well-qualified teachers. Opportunities for the study of photography, &c., are to be continued this Session. Full particulars of the classes are to be obtained from C. Smith, Organising Secretary. An organised Day Science School for Boys and Girls is now in full operation. A special course of lectures on Agriculture, Hygiene, and Physiology is arranged for the coming Session.

Battersea Polytechnic Institute.—This Institute has been built and equipped at a cost of over £55,000, the greater part of which has been raised by voluntary subscriptions. It is at present in possession of a fixed endowment of £2500 per year from the City Parochial Foundation. The London County Council also contributes an annual sum, estimated to amount to about £2500. It is under the direction of a Governing Body consisting of representatives of the South London Polytechnics Committee, the City Parochial Foundation, the London County Council, and the London School Board. The principal work of the Institute is the provision of Evening Classes for both sexes in all subjects of Technology, Pure and Applied Science, Art, Commerce, Domestic Economy,

and Music; but it also provides a Technical and Science Day School for Boys and Girls, a Training School of Domestic Economy, and a Domestic Economy School for Girls. During the last Session, 1894-95, the Evening Classes were attended by over 2930 persons, while 160 students were in regular attendance at the Day Schools. The Institute is provided with well equipped workshops, and also with laboratories for Engineering and Mechanics, Electrical Engineering, Physics, Chemistry, and Natural Science. Classes will commence on September 23rd.

CHEMICAL LABORATORY, WIESBADEN, GERMANY.

Director—Prof. R. FRESSENIUS, Ph.D.

Practical Instruction in the Laboratory Prof. R. FRESSENIUS, Ph.D.
.. .. . Prof. H. FRESSENIUS, Ph.D.
.. .. . W. FRESSENIUS, Ph.D.
.. .. . E. HINTZ, Ph.D.

LECTURES.

Experimental Chemistry (Inorganic) .. Prof. H. FRESSENIUS, Ph.D.
Experimental Physics W. FRESSENIUS, Ph.D.
Stoichiometry E. HINTZ, Ph.D.
Organic Chemistry L. GRUNHUT, Ph.D.
Chemical Technology W. LENZ, Ph.D.
Microscopy, with exercises in Microscopic work Prof. H. FRESSENIUS, Ph.D.
.. .. . W. FRESSENIUS, Ph.D., and
.. .. . E. HINTZ, Ph.D.
Chemistry and Analysis of Foods .. Dr. med. G. FRANK.
Hygiene J. BRAHM.
Practical exercises in Bacteriology ..
Technical Drawing, with exercises ..

The next Session commences on the 15th of October. The Regulations of the Laboratory and the Syllabus of Lectures will be forwarded gratis on application to C. W. KREDEL's Verlag, at Wiesbaden, or to the undersigned.

Prof. R. FRESSENIUS, Ph.D.

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Session 1895-96 commences on TUESDAY OCTOBER 1st. ENTRANCE EXAMINATION begins on Tuesday, September 24th.

For CALENDAR (price 1s. 4d. by post), containing detailed syllabuses of each course, particulars of fees, scholarships, &c., apply to

JOHN YOUNG, B.Sc.,
38, Bath Street, Glasgow. Secretary.

NOTICE TO ANALYSTS AND LABORATORY DIRECTORS.

BEST METHYLATED SPIRIT, manufactured by A. & J. WARREN, Wholesale Druggists, Dealers in Chemicals for Analytical Work, and Methylated Spirit Makers, 23 and 24, Redcliff Street, Bristol. For Four-pence a Pamphlet on Methylated Spirit, written by Algernon Warren, is obtainable from the Publisher, J. W. ARROWSMITH, Quay Street, Bristol; and SIMPKIN, MARSHALL, HAMILTON, KENT, and Co., Ltd., London.

THE CHEMICAL NEWS.

VOL. LXXII., No. 1870.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION. IPSWICH, 1895.

By Prof. RAPHAEL MELDOLA, F.R.S., F.I.C., FOR. SEC. C.S.,
President of the Section.

(Concluded from p. 148).

PROTOPLASMIC THEORY OF VITAL SYNTHESIS.

THE supposition that chemical synthesis in the organism is the result of the combination of highly complex molecules with simpler molecules, and that the unstable compounds thus formed then undergo decomposition with the formation of new products, may be provisionally called the protoplasmic theory of vital synthesis. From this standpoint many of the prevailing doctrines will have to be inverted, and the formation of the more complex molecules will be considered to precede the synthesis of the less complex. It may be urged that this view simply throws back the process of vital synthesis one stage, and leaves the question of the origin of the most complex molecules still unexplained. I grant this at once; but in doing so I am simply acknowledging that we have not yet solved the enigma of life. We are in precisely the same position as is the biologist with respect to abiogenesis, or the so-called "spontaneous generation." To avoid possible misconception let me here state that the protoplasmic theory in no way necessitates the assumption of a special "vital force." All that is claimed is a peculiar, and at present to us mysterious, power of forming high-grade chemical combinations with appropriate molecules. It is not altogether absurd to suppose that this power is a special property of nitrogen in certain forms of combination. The theory is but an extension of the views of Kühne, Hoppe-Seyler, and others, respecting the mode of action of enzymes. Neither is the view of the degradational origin of synthetical products in any way new.* I merely have thought it desirable to push it to its extreme limit in order that chemists may realise that there is a special chemistry of protoplasmic action, while the physiologists may exercise more caution in representing vital chemical transformations by equations which are in many cases purely hypothetical, or are based on laboratory experiments which do not run parallel with the natural process. The chemical transformations which go on in the living organism are thus referred back to a peculiarity of protoplasmic matter, the explanation of which is bound up with the inner mechanism of the process of assimilation. If, as the protoplasmic theory implies, there must be combination of living protoplasm with appropriate compounds before synthesis is possible, then the problem resolves itself into a determination of the conditions which render such combination possible,—i. e., the conditions of assimilation. It may be that here also light will come from the stereochemical hypothesis. The first step was taken when Pasteur found that organised ferments had the power of discriminating between physical isomerides; a similar selective power has been shown to reside in enzymes by the researches of Emil Fischer and

his coadjutors. Fischer has quite recently expressed the view that the synthesis of sugars in the plant is preceded by the formation of a compound of carbon dioxide, or of formic aldehyd, with the protoplasmic material of the chloroplast, and similar views have been enunciated by Stohmann. The question has further been raised by van 't Hoff, as well as by Fischer, whether a stereochemical relationship between the living and dead compounds entering into combination is not an absolutely essential condition of all assimilation. The settlement of this question cannot but lead us onwards one stage towards the solution of the mystery that still surrounds the chemistry of the living organism.

RECENT DISCOVERIES OF GASEOUS ELEMENTS.

The past year has been such an eventful one in the way of startling discoveries that I must ask indulgence for trespassing a little further upon the time of the Section. It was only last year, at the Oxford meeting of the British Association, that Lord Rayleigh and Prof. Ramsay announced the discovery of a gaseous constituent of the atmosphere which had up to that time escaped detection. The complete justification of that announcement is now before the world in the paper recently published in the *Philosophical Transactions of the Royal Society*. The history of this brilliant piece of work is too recent to require much recapitulation. I need only remind you how, as the result of many years' patient determinations of the density of the gases oxygen and nitrogen, Lord Rayleigh established the fact that atmospheric nitrogen was heavier than nitrogen from chemical sources, and was then led to suspect the existence of a heavier gas in the atmosphere. He set to work to isolate this substance, and succeeded in doing so by the method of Cavendish. In the meantime Prof. Ramsay, quite independently, isolated the gas by removing the nitrogen by means of red-hot magnesium, and the two investigators, then combining their labours, followed up the subject, and have given us a memoir which will go down to posterity among the greatest achievements of an age renowned for its scientific activity.

The case in favour of argon being an element seems to be now settled by the discovery that the molecule of the gas is monatomic, as well as by the distinctness of its electric spark spectrum. The suggestion put forward soon after the discovery was announced, that the gas was an oxide of nitrogen, must have been made in complete ignorance of the methods by which it was prepared. The possibility of its being N_2 has been considered by the discoverers and rejected on very good grounds. Moreover, Peratoner and Oddo have been recently making some experiments in the laboratory of the University of Palermo with the object of examining the products of the electrolysis of hydrazoic acid and its salts. They obtained only ordinary nitrogen, not argon, and have come to the conclusion that the anhydride $N_3.N_3$ is incapable of existence, and that no allotropic form of nitrogen is given off. It has been urged that the physical evidence in support of the monatomic nature of the argon molecule, viz., the ratio of the specific heats, is capable of another interpretation—that argon is, in fact, an element of such extraordinary energy that its atoms cannot be separated, but are bound together as a rigid system which transmits the vibrational energy of a sound-wave as motion of translation only. If this be the state of affairs we must look to the physicists for more light. So far as chemistry is concerned, this conception introduces an entirely new set of ideas, and raises the question of the monatomic character of the mercury molecule which is in the same category with respect to the physical evidence. It seems unreasonable to invoke a special power of atomic linkage to explain the monatomic character of argon, and to refuse such a power in the case of other monatomic molecules like mercury or cadmium. The chemical inertness of argon has been referred also to this same power of self-combination of its atoms. If this explana-

* See, e. g., Vines's "Lectures on the Physiology of Plants," pp. 145, 216, 227, 233, and 234. Practically all the great classes of synthetical products are regarded as the results of the destructive metabolism of protoplasm. A special plea for protoplasmic action has also been urged, from the biological side, by W. T. Thiselton-Dyer, *Journ. Chem. Soc.*, 1893; *Trans.*, pp. 680, 681.

tion be adopted it carries with it the admission that those elements of which the atoms composing the molecule are the more easily dissociated should be the more chemically active. The reverse appears to be the case if we bear in mind Victor Meyer's researches on the dissociation of the halogens, which prove that under the influence of heat the least active element, iodine, is the most easily dissociated. On the whole, the attempts to make out that argon is polyatomic by such forced hypotheses cannot at present be considered to have been successful, and the contention of the discoverers that its molecule is monatomic must be accepted as established.

In searching for a natural source of combined argon Professor Ramsay was led to examine the gases contained in certain uranium and other minerals, and by steps which are now well known he has been able to isolate helium, a gas which was discovered by means of the spectroscopic in the solar chromosphere, during the eclipse of 1868, by Professors Norman Lockyer and E. Frankland. In his Address to the British Association in 1872 (*Reports*, 1872, p. lxxiv) the late Dr. W. B. Carpenter said:—

"But when Frankland and Lockyer, seeing in the spectrum of the yellow solar prominences a certain bright line not identifiable with that of any known terrestrial flame, attribute this to a hypothetical new substance which they propose to call helium, it is obvious that their assumption rests on a far less secure foundation, until it shall have received that verification which, in the case of Mr. Crookes's researches on thallium, was afforded by the actual discovery of the new metal, whose presence had been indicated to him by a line in the spectrum not attributable to any substance then known."

It must be as gratifying to Professors Lockyer and Frankland as it is to the chemical world at large to know that helium may now be removed from the category of solar myths and enrolled among the elements of terrestrial matter. The sources, mode of isolation, and properties of this gas have been described in the papers recently published by Professor Ramsay and his colleagues. Not the least interesting fact is the occurrence of helium and argon in meteoric iron from Virginia, as announced by Professor Ramsay in July (*Nature*, vol. lli., p. 224). Like argon, helium is monatomic and chemically inert, so far as the present evidence goes. The conditions under which this element exists in cleveite, uraninite, and the other minerals, have yet to be determined.

Taking a general survey of the results thus far obtained, it seems that two representatives of a new group of monatomic elements characterised by chemical inertness have been brought to light. Their inertness obviously interposes great difficulties in the way of their further study from the chemical side; the future development of our knowledge of these elements may be looked for from the physicist and spectroscopist. Prof. Ramsay has not yet succeeded in effecting a combination between argon or helium and any of the other chemical elements. M. Moissan finds that fluorine is without action on argon. M. Berthelot claims to have brought about a combination of argon with carbon disulphide and mercury, and with "the elements of benzene, . . . with the help of mercury," under the influence of the silent electric discharge. Some experiments which I made last spring with Mr. R. J. Strutt with argon and moist acetylene submitted to the electric discharge, both silent and disruptive, gave very little hope of a combination between argon and carbon being possible by this means. The coincidence of the helium yellow line with the D₃ line of the solar chromosphere has been challenged, but the recent accurate measurements of the wave-length of the chromospheric line by Prof. G. E. Hale, and of the line of terrestrial helium by Mr. Crookes, leave no doubt as to their identity. Both the solar and terrestrial lines have now been shown to be double. The isolation of helium has not only furnished another link proving community of matter, and, by inference, of origin between the earth and sun, but an extension of the work by Professor

Norman Lockyer, M. Deslandres, and Mr. Crookes has resulted in the most interesting discovery that a large number of the lines in the chromospheric spectrum, as well as in certain stellar spectra, which had up to the present time found no counterparts in the spectra of terrestrial elements, can now be accounted for by the spectra of gases contained with helium in these rare minerals. The question now confronts us, Are these gases members of the same monatomic inert group as argon and helium? Whether, and by what mechanism, a monatomic gas can give a complicated spectrum is a physical question of supreme interest to chemists, and I hope that a discussion of this subject with our colleagues of Section A will be held during the present meeting. That mercury is capable under different conditions of giving a series of highly complex spectra can be seen from the memoir by J. M. Eder and E. Valenta, presented to the Imperial Academy of Sciences of Vienna, in July, 1894. With respect to the position of argon and helium in the periodic system of chemical elements, it is, as Professor Ramsay points out, premature to speculate until we are quite sure that these gases are homogeneous. It is possible that they may be mixtures of monatomic gases, and in fact the spectroscopic has already given an indication that they contain some constituent in common. The question whether these gases are mixtures or not presses for an immediate answer. I will venture to suggest that an attack should be made by the method of diffusion. If argon or helium were allowed to diffuse fractionally through a long porous plug into an exhausted vessel there might be some separation into gases of different densities, and showing modifications in their spectra, on the assumption that we are dealing with mixtures composed of molecules of different weights.

THE REFRACTION AND VISCOSITY OF ARGON AND HELIUM.*

By The Right Hon. Lord RAYLEIGH, Sec.R.S.

As compared with dry air, the refraction ($\mu - 1$) of argon is 0.961 and that of helium (prepared by Prof. Ramsay) is as low as 0.146.

Dry air being again taken as the standard, the viscosity of argon is 1.21, and that of helium is 0.96.

ON THE PRESENCE OF ARGON AND OF HELIUM IN CERTAIN MINERAL WATERS.

By Dr. C. H. BOUCHARD.

THE escape of very fine gaseous bubbles occurring in certain sulphuretted waters from the Pyrenees has been observed long ago. It begins a short time after such water has been drawn, and continues for a time variable according to the springs, sometimes for hours. In these waters, rendered slightly alkaline by sodium sulphide and silicate, these gases can neither be oxygen nor carbonic acid. It has been admitted, doubtless in consequence of the negative character of this substance, that it can only be nitrogen.

Spanish physicians have especially fixed their attention on this feature. They have named the waters which evolve nitrogen "azoades." They are found on the Spanish slope of the Pyrenees at Panticosa. On the French slope they are found at several stations, especially at the medicinal springs of Bagnères-de-Bigorre and at Cauterets, at the source of the Raillière.

* Read before the British Association (Section B), Ipswich Meeting, 1895.

Other springs in the Pyrenees which do not show any effervescence allow at intervals the escape of large bubbles of gas which are also considered as nitrogen.

During a recent stay at Cauterets, I had the curiosity to collect information of the gases which occasion these two kinds of phenomena. I succeeded in collecting somewhat considerable quantities of these gases at the point of issue, before any contact with the atmosphere, at the source of the Raillière and at two of the springs which feed the source of the Bois.

I have, thanks to the kindness of M. du Perron, the director of the waters, been enabled to examine the gas extracted from the bottled water of the Raillière, obtained by means of the mercurial pump, and also by ebullition.

Our colleague, M. Troost, who was present at my first experiments, has kindly offered his assistance for the determination of the physical and chemical characters of these gases, and the results which I now communicate to the Academy have been obtained with his assistance and under his direction.

These gases, when dried over potassa and phosphoric anhydride, have the characters of nitrogen; if heated to redness over magnesium wire for forty-eight hours, they lose their original volume. At the same time the wire is covered with a yellow layer, which on exposure to the air becomes white and evolves ammonia.

If the gas thus reduced is introduced into Plücker tubes with magnesium wires, and if under a low pressure, and with an effluve capable of heating the magnesium sufficiently, we exhaust the last traces of nitrogen (the spectrum of which disappears), we observe that the residual gases from the different springs are not identical.

The gases collected at the spring of the Raillière or extracted by boiling the waters of the same spring have given the characteristic rays of argon as well as those of helium.

The gases collected at the springs of the source of the Bois have all given both the characteristic rays of helium.

The gases collected at one of the two springs of the Bois (the one having the lowest temperature) lead us to suspect, on account of the abundance of rays in the red and the orange, that they contain some other element along with helium.

In our present ignorance of the physiological properties of argon and helium, we may ask if there is any relation between the medicinal properties of the waters of the Pyrenees and the composition of the gases which they evolve. The fact seems to me improbable.

The idea proposed twenty-five years ago by the Spanish physicians that the "azoades" owe their virtues to the nitrogen which they evolve has been abandoned. May these virtues, in default of nitrogen, depend on gases which are chemically less active than nitrogen, and which are present in the waters in a smaller proportion? It is, strictly speaking, possible; but the question ought not even to be raised if it is demonstrated that these gases are found also, and in analogous proportions, in the waters which flow or remain on the surface of the earth, and which serve us for dietetic purposes.

We are not absolutely certain concerning the origin of all the gases of mineral waters, and it may be that those with which we are concerned have their origin in the air carried down into deeper regions by the superficial waters. These waters, after being alkalisied by a sulphide, may re-ascend towards the surface necessarily deprived of oxygen and carbonic acid, and containing merely nitrogen and argon. Nevertheless, it seems at present that to the possible atmospheric origin of a part of the argon, and perhaps of the helium, there must be added some subterranean action, since if one of our springs contains both gases, another contains only helium, and a third contains along with helium something which is not argon.

The investigation which we have just made involves a research into the composition of the gases contained in waters on the surface of the earth. The results of this

study, which is in progress, will be communicated to the Academy.—*Comptes Rendus*, cxxi., p. 392.

THE COMBINATION OF MAGNESIUM WITH ARGON AND HELIUM.

By L. TROOST and L. OUVREARD.

If it is requisite to examine if there exists argon or helium in nitrogen gas it is not indispensable to pass the mixture over magnesium heated to redness or over lithium heated to dull redness in order to absorb the larger part of the nitrogen before causing the effluve to act on the gaseous mixture. The use of Plücker tubes with magnesium wire and a Ruhmkorff coil fitted with a Marcel Deprez interrupter, enables us to act at once upon a mixture containing only very small proportions of argon and helium.

This we have observed especially with the gases collected by Dr. Bouchard at the spring at the source of the Raillière, and at those of the Bois (at Cauterets).

We may at once introduce the dried gases into Plücker tubes with magnesium wires, and pass into them strong effluves. The nitrogen is only slowly absorbed at first, but when the pressure is sufficiently decreased the temperature of the magnesium wires rises sufficiently to occasion a commencement of evaporation which gives a metallic deposit in the state of a mirror on the glass of the tube around the wires. The combination of nitrogen with the magnesium vapour, which takes place with extreme rapidity, and the spectrum of nitrogen disappears. After this moment, the red rays characteristic of argon may be distinctly seen, or the red ray, D_4 , and the other rays characteristic of helium.

The brightness of these spectra may be increased by introducing at intervals fresh quantities of the gas into the Plücker tube, fitted with a good glass cock, and passing in again strong effluves.

If we continue the passage of strong effluves for some hours, the luminous intensity of the rays diminishes by degrees, and a complete vacuum is formed. The argon and helium which do not seem to combine in a sensible manner with magnesium heated to redness, combine with this metal, or rather with its vapour, under the prolonged influence of powerful effluves.

As Berthelot as pointed out, the use of the effluve constitutes the most effective procedure to determine these combinations.

In argon, platinum presents phenomena of evaporation and combination analogous to those presented by magnesium.—*Comptes Rendus*, cxxi., p. 394.

SOME REACTIONS OF FORMALDEHYD.

By T. H. LEE.

FORMALIN (40 per cent formaldehyd) from Schering, of Berlin, was taken.

Potassium permanganate immediately reduced. The formaldehyd fully oxidised to CO_2 and water. Ferric chloride solution (hot) is somewhat deepened in colour when formaldehyd is added. On allowing to cool, then re-heating and adding a little ammonium hydrate, a bulky red precipitate of basic ferric formate appears.

Ammoniacal silver solution appears to be reduced in two stages, viz. :—

1. $\text{Ag}_2\text{O} + \text{H.COH} = \text{Ag}_2 + \text{H.CO}_2\text{H}$. In this stage the silver falls in the specular form.
2. $\text{Ag}_2\text{O} + \text{H.CO}_2\text{H} = \text{Ag}_2 + \text{H}_2\text{O} + \text{CO}_2$. In this stage the silver falls in a pulverulent form.

A hot solution of potassium ferricyanide was made ammoniacal and a little formalin and sulphate of copper solution added. A brown precipitate immediately ap-

peared. The same reagents minus the formalin gave a fine green solution. This I regard as evidence of the reduction of ferricyanide to ferrocyanide.

Hot Fehling's solution is rapidly reduced by formaldehyde.

Ammoniacal copper sulphate *per se* is not reduced. Mercuric chloride is not reduced.

Alkaline mercurio-potassium iodide is immediately reduced to metal in the cold.

Edgcombe Villa, Clevedon.

ON THE REFRACTION AND DISPERSION OF LIQUID OXYGEN.*

By Professors LIVEING and DEWAR.

In August, 1892, we published in the *Philosophical Magazine* (vol. xxxiv., p. 208) a measure of the refractive index of liquid oxygen at its boiling-point for the yellow sodium rays, made by means of a prism. In the following year (vol. xxxvi., p. 330) we published a measure of the same quantity made by a different method. For the reasons stated, we could only obtain measures more or less approximate to the truth. Since then we have made several attempts, but hitherto in vain, to make hollow prisms with vacuous jackets, in which the liquid oxygen could be kept in a tranquil state while the observations were going on. We have also attempted unsuccessfully other methods of taking the measures.

The chief difficulties which we encountered in making our former measures arose from the irregularities and striations of the glass vessels, and from the continual ebullition of the liquid oxygen. These difficulties have now been to a great extent obviated. We have come back to the method we used in 1893, which we then described as the method of MM. Terquem and Trannin, but which had previously been suggested by Prof. E. Wiedemann (*Archives de Genève*, li., p. 340, 1874). However, for the cylindrical vessel before used we substituted a globular vessel having the inside of its vacuous jacket silvered all over except a narrow vertical strip about 4 m.m. wide, which was left unsilvered to allow of the passage of light. This vessel was used, exactly as the cylindrical vessel had been used in the former experiments, as a lens by which an image of a source of light was thrown on to the slit of a spectroscope. The pair of glass plates, separated by a thin stratum of air and fixed to a rod which was the prolongation of the vertical axis of a theodolite, were arranged at about the centre of the globe. The oxygen in the globe was very tranquil, and the silvering cut off all light which did not pass nearly centrally through the globe. The result was that the light of the rays observed was cut off, when the glass plates were turned through the proper angle, much more sharply than before, and the measures are so much more trustworthy.

We found the spark between cadmium electrodes a convenient source of light, both because the rays are bright, and because they are dispersed through a considerable range in the visible spectrum, and it was possible to watch their extinction one after another as the glass plates were slowly turned. Even with this arrangement the extinction of the rays when liquid oxygen was in the globe was not quite so sharp as when the experiment was made with alcohol. This was probably due to the scattered light from the bubbles in the oxygen, and was more troublesome in regard to the brightest rays.

We obtained, as the mean of several observations, for the blue ray of cadmium, $\lambda 4416$, $\mu = 1.2249$; for the red ray, $\lambda 6438$, $\mu = 1.2211$; for the green ray of thallium, $\lambda 535$, $\mu = 1.2219$. Also, by using a flame, we obtained

for the red ray of lithium, $\lambda 6705$, $\mu = 1.2210$, and for the yellow rays of sodium, $\lambda 5892$, $\mu = 1.2214$.

The last figure is less than we had found in 1892 by the prism method, which was 1.2236, and still less than that found in 1893, which was 1.226. It is also less than that recently found by Olzowski and Witowski, (*Bull. de l'Acad. de Cracovie*, July, 1894, p. 246), which was between 1.2222 and 1.2235. The values we have now found for the refractive indices corresponding to the red ray of lithium and the green ray of thallium are also less than those found by Olzowski and Witowski, which were about 1.2213 and 1.2235 respectively. We think, however, that our measures for the red and blue rays of cadmium are better than those made for the thallium and sodium rays.

These give, for the mean green, μ nearly equal to 1.222, and, taking the density of oxygen at its boiling-point as 1.137, the refraction-constant by Gladstone's formula—

$$\frac{\mu - 1}{d} = 0.1953,$$

and by Lorenz's formula—

$$\frac{\mu^2 - 1}{(\mu^2 + 2)d} = 0.1242.$$

Taking Regnault's value for the density of oxygen gas at 0° and 76 c.m., viz., 0.00143, and Mascart's value for the mean refractive index, viz., 1.000271, we find for gaseous oxygen the refraction-constant—

$$\frac{\mu - 1}{d} = 0.18947,$$

and—

$$\frac{\mu^2 - 1}{(\mu^2 + 2)d} = 0.12631.$$

It will be seen that this last is nearly equal to the refraction-constant as above determined for the liquid,

In Mascart's paper "Sur la Refraction des Gaz" (*Annales l'Ecole Normale Experimental*, 1876) some observations on the "Dispersion of Oxygen and other Gases" were given, which enable a comparison to be made between this property in the gaseous and liquid states. Taking Cauchy's formula—

$$n - 1 = a \left(1 + \frac{b}{\lambda^2} \right)$$

then—

$$\frac{n' - n}{n + 1} = b \frac{\frac{1}{\lambda^2} - \frac{1}{\lambda'^2}}{1 + \frac{b}{\lambda^2}}$$

From this b is calculated by Mascart, and is called the Coefficient of Dispersion. The blue and red cadmium lines represent the extremest difference of wave-lengths employed. This gave for oxygen the maximum and minimum values 0.0049 and 0.0078, and mean value 0.0064 for the Constant of Dispersion. Taking the values for the liquid state given above, the value of b becomes 0.0064. It seems, therefore, that the Dispersion Constant in the liquid state is identical with that of the gas.

The Examinational System.—At the recent Congress of the Society of Chemical Industry, held at Leeds, July 31st to August 2nd, Dr. T. E. Thorpe, F.R.S., in his Presidential Address, expressed the timely opinion that we need institutions of research where young men, no longer haunted by the spectra of the ever-threatening examination, may find time and scope to practise their minds in real investigations and try their powers in attempts to promote Science and extend its domain.

* From the *Philosophical Magazine* for September.

CALAVERITE FROM CRIPPLE CREEK,
COLORADO.*

By W. F. HILLEBRAND.

THE occurrence of tellurium in the ores of the mining district of Cripple Creek, Colorado, has been known from an early day in the as yet brief industrial history of that region. That it was, in part at least, associated with gold was likewise known from the observance of a crystallised gold-tellurium mineral. Although the ores of the district are chiefly gold carriers, they contain also a little silver, and since recognised silver minerals had not been observed, or at most only in minute amount, it seemed probable that the silver was associated with the gold in the tellurium compound. Indeed, Mr. R. Pearce, of Denver, came to the conclusion, from his examination (*Proc. Colo. Sci. Soc.*, Jan. 8 and April 5, 1894) of certain ore concentrates, that this mineral was sylvanite. It is, however, of very sparing occurrence, so that it was only by dint of much effort that material in sufficient purity for decisive tests was obtained by Prof. R. A. F. Penrose, jun., who transferred it to me for chemical examination. The material was derived from three different mines in order to ascertain whether it was of constant or varying composition, or, in fact, whether there might not be more than one specific telluride. That the composition does vary within narrow limits the analyses show, but there is no reason apparent for assuming more than one species.

The material from the Prince Albert mine, the first received, was with little trouble brought into an almost ideal condition of purity. It was in part apparently fairly well crystallised, but the measurements made by Prof. S. L. Penfield, of New Haven, are unfortunately not decisive as to the system of crystallisation, as shown by his notes at the close of this paper. The specific gravity of this material was 8.91 at 24°C., which becomes 9.00 when corrected for a small admixture of silico-ferruginous gangue of assumed specific gravity 2.70 (probably low). The other samples were imperfectly crystallised and held too much foreign matter of uncertain composition to make specific gravity determinations of any value.

Analyses of Calaverite.

	I. Prince Albert mine.	II. Raven mine.	III. C. O. D. mine.
Tellurium (Te) ..	57.27	47.69	53.89
Gold (Au) ..	38.95	33.93	39.31
Silver (Ag) ..	3.21	1.47	0.85
Insoluble ..	0.33	5.80	0.91
Ferric oxide (Fe ₂ O ₃) ..	0.12 (a)		
Iron (Fe) ..		5.41	1.67
Sulphur (S) ..		6.17 (b)	1.58 (2.96 FeS ₂)
Manganese (Mn) ..			0.23 (c)
Calcium (Ca) ..			0.51
Magnesium (Mg) ..			0.10
Oxygen, fluorine, and soluble silica, by difference ..			0.95 (d)
	99.88	100.47	100.00

(a) This was included with the insoluble matter in arriving at the corrected density.

(b) Calculated from the Fe to make FeS₂.

(c) As MnO₂?

(d) A part of the calcium found in solution was derived from fluorite, which likewise constituted some of the soluble matter in this instance.

Selenium has been reported to occur in traces in the district (F. C. Knight, *Proc. Colo. Sci. Soc.*, Oct. 1, 1894), but it could not be detected in the amount of mineral taken for the above analyses.

Excluding everything but gold, silver, and tellurium, and re-calculating to 100, the following comparison is obtained:—

	I. Ratio.	II. Ratio.	III. Ratio.
Te ..	57.60	57.40	57.30
Au ..	39.17	40.83	41.80
Ag ..	3.23	1.77	0.90
	100.00	100.00	100.00

The ratio here obtaining is that for sylvanite and calaverite, but the very low percentage of silver shows that the mineral is calaverite. Indeed, the first analysis agrees almost exactly with Genth's analysis of the species. Interesting is the slight variation in the ratio between gold and silver, and the very low percentage of silver in the mineral from the C. O. D. and Kaven mines. Calaverite, the lowest silver carrier of the gold-silver tellurides, has not heretofore been known to carry less than 3 per cent of silver.

The pyrognostic characteristics of the mineral from the Prince Albert mine were essentially those ascribed to calaverite. In the closed tube it fuses, giving a white coating near the assay, and a globular grey coating just above, which latter by strong heat can be in part driven higher up, leaving the glass covered with the same white fused coating as lower down. This latter is yellow while hot. On charcoal the mineral fuses with a green flame, giving a white coating and similar fumes, and leaving a yellow bead. The colour is pale bronze yellow, in powder greenish grey. The hardness is not less than and perhaps a little over 3. Specific gravity, as given above, 9.00.

The identity of the telluride occurring at Cripple Creek, which in oxidising gives free gold and oxidised tellurium compounds,* seems thus satisfactorily established, but unless there is another richer in silver the mode of occurrence of the silver in some of the ores is still in large part unaccounted for. It may be derived from a very rich argentiferous tetrahedrite of which Prof. Penrose submitted a small specimen for identification. This carries over 11 per cent of silver, but is said to be excessively scarce, and therefore hardly to be considered in this connection, unless indeed this should have been the original source of most of the silver and later have suffered oxidation to a great extent, whereby the silver has become more evenly distributed throughout the ore.

Professor Penfield has kindly contributed the following notes on the crystallography of the mineral:—

"The crystals of calaverite which were examined were developed with prismatic habit, but the prismatic zone was striated to such an extent that it was impossible to identify a single face in the zone, and on the reflecting goniometer almost an unbroken band of signals was obtained in a revolution of 360°. Owing to oscillatory combinations the crystals were also much distorted, so that they did not present regular cross sections.

The prisms were attached so that doubly terminated ones were not observed, while the faces at the free end were small and developed with so little symmetry that after a study of a number of crystals it was found impossible to determine with certainty the system of crystallisation.

The crystals do not exhibit the perfect cleavage ascribed to sylvanite and krennerite, but are similar to the former in some of their angles. When placed in position to show their relation to sylvanite they have their prismatic development parallel to the *b* axis. One crystal, which owing to its development was more carefully measured than any of the others, was apparently a twin about 101, and showed at the end the forms 111 and 110. The measurements compared with the corresponding ones of sylvanite are as follows:—

* From tests made by myself on a number of specimens collected by Prof. Penrose the combination seems to be chiefly, if not altogether, with iron, but whether as tellurite or tellurate could not be ascertained.

* From the *American Journal of Science*, vol. 1., August, 1895.

	Sylvanite.		
III $\wedge$ (III) over twinning plane	93° 35'	94° 30'	
III $\wedge$ (III) " "	35 2	34 43	
III $\wedge$ III	36 35	37 3	
III $\wedge$ III in twin crystal	36 33	37 3	

Other forms which were measured could not be referred to the sylvanite axes, and it seems probable from their development and lack of symmetry that the crystals are triclinic; but no satisfaction was obtained after a long and careful study of the limited supply of material on hand.

In conclusion, therefore, it may be stated that the crystals are probably triclinic, but near sylvanite in angles and axial ratio."

THE REDUCTION OF THE ACIDS OF SELENIUM BY HYDRIODIC ACID.*

By F. A. GOOCH and W. G. REYNOLDS.

A METHOD for the iodometric determination of selenious acid has been recently announced by Muthmann and Schaefer (*Berichte d. D. Chem. Gesell.*, xxvi., 1008) which is based upon the reduction of selenious acid by hydriodic acid and the direct titration of the iodine thus liberated. To determine the selenious acid it is only necessary to add it in solution to an acidulated solution of potassium iodide, when iodine and selenium are both set free in elementary form, the former being directly determinable by titration with sodium thiosulphate after addition of starch. The difficulty in the process is said to be the uncertainty as to the exact point in the titration at which the starch blue disappears from the liquid in which the finely divided and opalescent selenium is held in suspension. For this reason the process is recommended for use only when great accuracy is not essential.

Evidently if the reaction between the acidulated iodide and selenious acid is single and complete, the process should be capable of improvement by removing the selenium before the titration is attempted. This we have succeeded in doing without difficulty. We find the most convenient and rapid way to remove the finely-divided selenium is to filter the liquid containing it by means of the vacuum pump upon a thick felt of asbestos in a perforated crucible or cone of large filtering surface. With a properly prepared filter of this description there is no difficulty in separating the selenium in a very few moments so completely that it is possible to determine the iodide remaining dissolved in the excess of potassium iodide with all the accuracy characteristic of this most exact of titration processes. We find, however, that when the difficulty of determining the end-reaction in the titration of the iodine by the thiosulphate is overcome, it becomes apparent that the reaction upon which Muthmann and Schaefer depend is not perfect. Either the reduction of the selenious acid to selenium is not complete, or else the iodine remains in combination to a slight extent with the selenium and so fails to appear in the filtrate. This is evident from the results of the experiments of Table I., in which the selenious acid and potassium iodide acidulated with hydrochloric acid were brought together, the liquid thrown upon the asbestos filter, the selenium washed until free from soluble iodine, and the filtrate containing the iodine treated as usual with sodium thiosulphate in presence of starch. The details of treatment are described sufficiently in the table. The selenium dioxide was prepared for the work from the so-called pure elementary selenium by dissolving it in strong nitric acid, evaporating off the excess of the last, treating the solution of the residue in water with barium hydroxide, filtering to remove selenic

acid formed in the oxidation and traces of sulphuric acid possibly present as an impurity, recovering the selenium dioxide by evaporation, and purifying it by subliming and re-subliming it in a current of dry air until it was clean and white.

TABLE I.

SeO ₂ taken. Grm.	KI used. Grms.	HCl used (Sp. gr. 1.20). C.m. ³	Volume before filtering. C.m. ³	SeO ₂ found. Grm.	Error. Grm.
0.0499	1	5	100	0.0479	0.0020—
0.0499	1	5	100	0.0477	0.0022—
0.2035	3	5	100	0.1896	0.0139—

From these figures it is plain that iodine was not found in the filtrate in amount corresponding to the selenium dioxide present. In the following experiments of Table II. an excess of the thiosulphate was added before filtering off the selenium so that there should be every opportunity for the iodine and thiosulphate to interact before the removal of the selenium. In two experiments the proportion of hydrochloric acid was increased ten-fold for the purpose of seeing whether the presence of a large amount of free acid influences the result.

TABLE II.

SeO ₂ taken. Grm.	KI used. Grms.	HCl used (Sp. gr. 1.20). C.m. ³	Volume before filtering. C.m. ³	SeO ₂ found. Grm.	Error. Grm.
0.0499	1	5	100	0.0489	0.0010—
0.0499	1	3	100	0.0485	0.0014—
0.0499	1	50	100	0.0489	0.0010—
0.0499	1	50	100	0.0488	0.0011—
0.2006	3	5	100	0.1925	0.0081—
0.2030	3	5	100	0.1945	0.0085—

These results show improvement over those obtained when filtration is made before adding with the thiosulphate, but it is obvious that the presence of a large proportion of free hydrochloric acid is without effect upon the reaction, and that the iodine set free and measured is still deficient in proportion to the amount of selenium dioxide present. Plainly the reduction of the selenium dioxide is incomplete, or else there is formed between the selenium and iodine a combination, such as was noticed by Hautefeuille (*Comptes Rendus*, lxxviii., 1554) in the interaction of iodine upon hydrogen selenide. In either case it should be possible to push the reaction farther toward completion by submitting the mixture of selenious acid, potassium iodide, and hydrochloric acid to distillation. We have used for this purpose an apparatus employed and described in connection with previous similar work in this laboratory. The distillation flask is a Voit gas-washing flask, and this is sealed to the inlet tube of a Drexel wash-bottle used as a receiver, to the outlet tube of which is sealed a Will and Varrentrapp absorption apparatus to serve as a trap. The mixture to be distilled was introduced into the flask, a solution of 3 grms. of potassium iodide in 100 c.m.³ of water was put into the receiver and trap and during the distillation a slow current of carbon dioxide was passed through the apparatus to keep the boiling regular. Naturally the acidified solution of the iodide in the flask retains with great tenacity traces of dissolved iodine, so that, in order to determine all the iodine liberated in the reaction, the residue in the flask as well as the distillate in the receiver and trap was titrated in the usual way with sodium thiosulphate. The details of treatment and the results are recorded in Table III.

These results are all fairly good, though all a little deficient, for amounts of selenium dioxide up to 0.2 grm.; but when the amount of the dioxide reaches 0.5 grm. the iodine found in the distillate and in solution in the residue falls far below the theory based upon the assumption that the products are selenium, iodine, and water. The selenium in the residue was left after the boiling in a dense

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. 1., Sept., 1895.

TABLE III.

SeO ₂ taken. Grms.	KI in flask. Grms.	HCl in flask. (Sp. gr. 1.20). C.m.s.	Total volume boiled. C.m.s.	Time in minutes.	SeO ₂ found. Grms.	Error. Grms.
0.0499	1	5	60	5	0.0497	0.0002-
0.0499	1	5	60	5	0.0497	0.0002-
0.0499	1	5	60	10	0.0496	0.0003-
0.2000	3	5	60	10	0.1995	0.0005-
0.2000	3	5	60	10	0.1991	0.0009-
0.2023	3	5	60	10	0.2018	0.0005-
0.5018	3	5	60	10	0.4635	0.0383-

crystalline condition in the experiments with the smaller amounts, so that it did not interfere with the titration of the free iodine; but in the last experiment, in which approximately 0.5 gram. of the dioxide was treated, the selenium remained in pasty form adhering to the flask. Subsequent examination proved that the pasty selenium held iodine, which was liberated slowly to water, and more rapidly to an aqueous solution of potassium iodide. The largest errors have been found (excepting that of the last experiment from the discussion) when the free iodine was filtered off from the reduced selenium; better results were obtained when the precipitated selenium was first treated with the thiosulphate before filtering; and in the distillation process the best approximations are made to true indications. It is obvious that as the proportion of selenium and iodine increase, the tendency to form a combination is more manifest. The error thus introduced in the determination of the selenium dioxide by the distillation process is allowable up to the limit of 0.2 gram.

Potassium iodide in hydrochloric acid acts much less readily upon selenic acid than upon selenious acid. When the hydrochloric acid is present in small proportions in the mixture of selenic acid and the iodide the reduction is very imperfect, but it tends to approach completion as the strength of hydrochloric acid is increased.

It is obvious, in the light of the previous experiments with selenious acid, that it is unreasonable to expect the full liberation of iodine in the action of selenic acid upon the iodine when the free iodine is not removed from the sphere of action as it is liberated. In the distillation process the case is otherwise, and there is no reason to anticipate that the determination of selenic acid should present greater difficulty than is encountered in treating selenious acid under similar circumstances. The experiments of Table IV., in which selenic acid (obtained by oxidising known amounts of selenium dioxide by means of potassium permanganate in the manner described in a previous paper from this laboratory—Gooch and Clemens, *Amer. Journ. of Science*, 1. 51) is treated according to the distillation method outlined above for the determination of selenious acid, show that this expectation is realised, and that the analytical results are fairly good.

TABLE IV.

SeO ₂ taken. Grms.	KI in flask. Grms.	HCl in flask. (Sp. gr. 1.20). C.m.s.	Total volume boiled. C.m.s.	Time in minutes.	SeO ₂ found. Grms.	Error. Grms.
0.0593	1	5	60	5	0.0593	0.0000
0.0593	1	5	60	5	0.0591	0.0002-
0.0593	3	5	60	10	0.0596	0.0003+
0.1779	3	5	60	10	0.1769	0.0010-
0.1779	3	5	60	10	0.1780	0.0001+
0.1779	3	5	60	10	0.1764	0.0015-

In conclusion, it is plain that while the simple contact of solutions of selenious acid or selenic acid and potassium iodide acidified with hydrochloric acid does not determine the liberation of the full amount of iodine which would be expected if selenium, iodine, and water were the sole products of action, it is possible to bring about such action with a close approximation to completeness, when the amounts of selenium present are not too large, by sub-

mitting such mixtures to distillation. We prefer, in applying the reaction to analytical purposes, to work with the apparatus and under the conditions described,—treating, preferably, not more than 0.2 gram. of the selenium oxide, using from 1 gram. to 3 grms. of potassium iodide in the distilling-flask with 5 c.m.s. of strong hydrochloric acid in a total volume of 60 c.m.s., and continuing to boil for ten minutes.

REPORT OF COMMITTEE ON ATOMIC WEIGHTS, PUBLISHED DURING 1894.*

By F. W. CLARKE.

(Continued from p. 106).

COBALT AND NICKEL.

THE atomic weights of these two metals have been re-determined by Winkler (*Zeit. Anorg. Chem.*, viii., 1), who adopts a radically new method, using the pure electrolytic elements as a starting-point. In each case the weighed metal, deposited upon platinum, is treated with a weighed excess of iodine dissolved in potassium iodide. The metals are thus converted into iodides, and the excess of iodine is then measured by titration with thiosulphate solution. Thus the direct ratios, Co : I, Ni : I, are determined. Two series of estimations are given for each metal, with results as follows. The atomic weights used in calculation are H = 1, I = 126.53.

First Series—Cobalt.

Wt. Co.	Wt. I.	At. wt. Co.
0.4999	2.128837	59.4242
0.5084	2.166750	59.3772
0.5290	2.254335	59.3828
0.6822	2.908399	59.3582
0.6715	2.861617	59.3824

Mean .. 59.3849

Second Series—Cobalt.

Wt. Co.	Wt. I.	At. wt. Co.
0.5185	2.200694	59.3798
0.5267	2.246037	59.3430
0.5319	2.268736	59.3294

Mean .. 59.3507

Mean of all, Co = 59.3678

First Series—Nickel.

Wt. Ni.	Wt. I.	At. wt. Ni.
0.5144	2.217494	58.6702
0.4983	2.148502	58.6918
0.5265	2.268742	58.7268
0.6889	2.970709	58.6828
0.6876	2.965918	58.6678

Mean .. 58.6878

Second Series—Nickel.

Wt. Ni.	Wt. I.	At. wt. Ni.
0.5120	2.205627	58.7436
0.5200	2.204107	58.7732
0.5246	2.259925	58.7432

Mean .. 58.7433

Mean of all, Ni = 58.7155.

For O = 16 these become—

Co = 59.517

Ni = 58.863.

(To be continued).

* From the *Journal of the American Chemical Society*, vol. xvii., No. 3. Read at the Boston Meeting, Dec. 28, 1894.

WARNING AGAINST THE USE OF FLUORIFEROUS HYDROGEN PEROXIDE IN ESTIMATING TITANIUM.

By W. F. HILLEBRAND.

DUNNINGTON (*Journ. Am. Chem. Soc.*, xiii., 210) has pointed out a source of error to be guarded against in estimating titanium in rocks and minerals by Weller's method, due, as he believes, to the partial reversion, in certain cases, of ordinary titanite to meta-titanic acid, which does not afford a yellow colour with hydrogen peroxide. It remains for me to indicate another source of error in the possible presence of fluorine in the hydrogen peroxide.

For two years the colorimetric method has given reasonable satisfaction in this laboratory, but recently a new lot of hydrogen peroxide was purchased, of a different brand from that hitherto used, and, after a time, it was noticed that the results obtained were in some instances far too high, and that no two determinations agreed.

It is known that hydrogen peroxide does not produce a yellow colour in titanium solutions carrying hydrofluoric acid or fluorides, and, moreover, the addition of even a drop of the dilute acid to an already peroxidised titanium solution weakens the colour. For this reason it is necessary to take the greatest care to ensure the complete expulsion of all fluorine when dissolving rocks or minerals by means of hydrofluoric and sulphuric acids prior to the colorimetric estimation. A drop of hydrofluosilicic acid acts similarly, but the latter reagent cannot be made to completely discharge the colour even if added in great excess.

This, however, was not suspected as the cause of our trouble until, on referring to the circular of one of the leading makers of hydrogen peroxide in America, whose product has always given satisfactory results in titanium work, it was found that among the various acids enumerated as usually to be found in the commercial article, hydrofluoric acid appears. Talbot and Moody, in the *Technology Quarterly*, v., 123, mention hydrofluosilicic acid as of frequent occurrence in the peroxide manufactured a few years ago. On examining the suspected peroxide by neutralising with fixed alkali, evaporating to dryness, and heating with strong sulphuric acid, fluorine was detected by the odour of the acid evolved and by its action on glass.

It is therefore imperative to use only hydrogen peroxide which is free from fluorine in estimating titanium, for its presence may utterly vitiate the results, even if only 2 or 3 c.c. of the peroxide are employed.—*Journal of the American Chemical Society*, xvii., No. 9.

DETERMINATION OF ANTIMONY AS ANTIMONIC ANTIMONIATE.

By OTTO BAUNEK.

THE method of determining antimony as antimonic antimoniate devised by Bunsen has for some time fallen into discredit, after having been formerly in almost universal use and being recommended in the last edition of the text-book of Fresenius as decidedly trustworthy. The cause is chiefly a subsequent publication of Bunsen's, in which he completely abandons as untrustworthy the method which he had previously recommended, and supersedes it by a new procedure—the determination of antimony as pentasulphide. According to his investigations the temperature of the decomposition of the tetroxide is not much higher than that of its formation, so that it is difficult to seize the point when the weight of the contents of the crucible corresponds to the tetroxide of the antimony taken. On continued ignition the weight of the crucible progressively diminishes, and even

0.1 grm. of the substance can be completely volatilised in six hours.

This observation is directly contradictory to the statements of most text-books and manuals of chemistry, even the most recent, which characterise the tetroxide as infusible and fixed on ignition. This contradiction, as well as the circumstance that the above method is still in extensive practice and has been recommended in various recent manuals of quantitative analysis, induced me to examine thoroughly the permanence of antimony tetroxide on ignition, and the consequent trustworthiness of the above method of determination.

Chemically pure antimony, obtained by reducing the purest potassium antimoniate with potassium cyanide,* was weighed off and oxidised with nitric acid, whilst the crucible was covered with a watch-glass. After the latter had been rinsed out the contents were evaporated to dryness, and the residue heated in an uncovered crucible—at first gently, and then at redness, until the weight is constant. The weight of the contents of the crucible exactly corresponded to the weight of the antimony employed as calculated from the formula Sb_2O_4 . The crucible was then left uncovered for several hours at a bright red-heat without the slightest loss of weight.

In this manner an entire series of determinations was effected with different quantities of antimony. Hence it appears that, on proceeding as above, the antimonic antimoniate can be used as a form of weighing antimony.

I then sought to ascertain under what conditions antimonic tetroxide may be volatilised on ignition.

A weighed quantity of antimony was oxidised in the manner above described, and ignited until the weight was constant. The lid of the crucible was then put on, and the ignition continued under otherwise similar conditions. On taking off the cover, after five minutes, its inside was found covered with shining needles of tetroxide, whilst a white fume ascended from the crucible, the weight of which had naturally considerably decreased. The sintered residue was then pulverised, weighed off in a porcelain crucible of equal size, and ignited again with the same flame but without cover. After ignition for an hour not the slightest decrease of weight was perceptible. If the ignition was then repeated in the covered crucible the former phenomenon reappeared, and there was again a sublimate of tetroxide on the inside of the lid.

As the tetroxide is persistent on ignition, even on the exclusion of air,—as it appears from its behaviour on ignition in a closed tube, when there appears not the slightest trace of a sublimate,—its decomposition into tetroxide and oxygen on ignition in a covered crucible can be referred only to the reductive action of the flame gases—an assumption which is verified by the following experiment:—

A porcelain crucible, such as was used in the previous experiment, was suspended in a circular disk of asbestos-pasteboard in such a manner as to include tightly the edge of the crucible. The antimonic acid was then converted into tetroxide by ignition in an open crucible until the weight was constant. The cover was then put on, and the crucible heated for one hour to bright redness without any loss of weight or the appearance of a trace of sublimed tetroxide. If the disk was then removed the same flame, in a very short interval, occasioned a strong reduction to tetroxide.

In this manner the volatilisation of antimony tetroxide—with decomposition into tetroxide and oxygen—as obtained by Bunsen is easily explained. The flame-gases are caught under the projecting edge of the cover of the crucible, displace the air in the interior of the crucible, and exert a reductive action. This is also the case if the flame does not enwrap the entire crucible, but merely

* This reduction can be effected without fear of an explosion if a small quantity of the mixed substances is fused in a capacious porcelain crucible, and the rest is added to the glowing melt in small portions, waiting each time until the violent reaction is at an end.

its lower part. But if the interior of the crucible can freely communicate with the atmospheric air, the action of the flame-gases is suppressed.

Volatilisation may also be avoided in a covered crucible if it is very large, and if the bottom only is touched by the point of the flame. But as, on evaporating the nitric acid, some of the substance generally adheres to the sides, this method of ignition is impracticable. We have now indeed found that—

1. On igniting antimoniac acid with access of air a constant weight is quickly reached.
2. The antimony oxide thus obtained corresponds to the formula Sb_2O_3 .

But I have further effected some determinations of antimony as tetroxide with previous precipitation of the antimony as sulphide, the results of which demonstrate the accuracy of the method.

In order to prevent an oxidation of the precipitate along with the filter, the washed antimony sulphide was rinsed with a little water into a small capsule, and the particles still clinging to the filter are dissolved in hot ammonium sulphide, which is easily effected whilst the precipitate is moist. The solution is evaporated to dryness in a weighed porcelain crucible; the main bulk of the precipitate is also rinsed into the crucible, and again evaporated. The precipitate is then moistened with concentrated nitric acid and oxidised with fuming nitric acid, using instead of the cover a watch-glass, which is then rinsed off. The solution is then evaporated to dryness, the sulphuric acid which has been formed is cautiously driven off by heat, and the residue strongly heated in an open crucible until the weight is constant. The method is, in accuracy, at least equal to the other methods of determining antimony, and surpasses them in simplicity and promptitude of execution.

In presence of small quantities of antimony, when the inaccuracies attending weighing a precipitate along with the filter have a considerable effect upon the result, Bunsen's old method may be considered preferable to all others.—*Zeit. Anal. Chem.*, xxiv., p. 171.

NOTICES OF BOOKS.

Poisons: Their Effects and Detection. A Manual for the Use of Analytical Chemists and Experts. With an Introductory Essay on the Growth of Modern Toxicology. By ALEXANDER WYNTER BLYTH, M.R.C.S., F.I.C., F.C.S., &c., Barrister-at-Law, Public Analyst for the County of Devon, and Medical Officer of Health and Public Analyst for St. Marylebone. Third Edition, Revised and Enlarged. With Tables and Illustrations. 8vo., pp. 724. London: Charles Griffin and Co., Ltd. 1895.

We have here before us an excellent treatise, instructive and suggestive, not merely to chemical experts and students, to medical practitioners and pharmacists, but to chemical manufacturers, to legislators, and lawyers, and, if we may presume to make the suggestion, even to novelists and play-wrights and to the writers of the daily press.

The work has already passed through two editions, but it has undergone such enlargements and revisions—in accordance with the advance of science—that it may fitly be treated as a new publication.

In the "Old Poison Lore" Mr. Blyth holds that the traditions of poisons which, though producing no immediate effect, might yet prove ultimately fatal, were more than fables. Have we not a too familiar instance of this phenomenon in the bite of a rabid dog? Our author thinks that "the Asiatic poisoners were well acquainted with the infectious properties of certain malignant diseases." It might be added that they selected poisons

whose effects might simulate the symptoms of natural disease.

In connection with the detection of poisoning, we may mention that it is to the Popes that science was indebted for the sanction, in the Fifteenth Century, to dissect human subjects.

The account given in the following chapter of the development of our modern methods for the detection of poisons in the body. As an epoch in toxicology is mentioned the discovery of the Marsh method of detecting arsenic, which "for the first time rendered the most tasteless and easily administered poison in the world at once the easiest of detection."

We come to that difficult question—the definition of poison. The author comments on the British law (Criminal Consolidation Act, 1861) the German statute, and the present French law. The author's own definition of poison, as given in the first edition of the present work, is—"A substance of a definite chemical composition, whether mineral or organic, may be called a poison if it is capable of being taken into any living organism and causes by its own inherent chemical nature impairment or destruction of function."

As to the classification of poisons, the author admits that no perfect classification is yet possible.

In considering the statistics of poisoning, the author holds that the higher the mental development of a nation the more likely are its homicides to be caused by subtle poison, and its suicides by chloral, morphine, or hemlock. The two leading poisons in South Britain for the decade ending 1892 are opiates and lead; carbolic acid coming third. Out of 1000 attempts in France to injure or destroy human life by poison, arsenic accounts for 331 and phosphorus for 301—two of the most painful poisons ordinarily available.

The connection between toxic action and chemical composition is discussed at some length. The researches of Dr. Blake and of Rabuteau on the comparative toxic action of metals seem to have been overlooked. The more attention has been given to the organic poisons. The author considers that the occurrence of hydroxyl appears frequently to confer poisonous properties upon the substance. In aromatic compounds the toxic power increases with the number of hydroxyls.

The substitution of a halogen for hydrogen is apt to produce narcotic substances. This section, and especially the general theory of Oscar Loew (p. 39), deserve the most careful study, experimental if possible.

The chapter on "Life Tests"—the identification of poisons by experiments on animals—has been greatly abridged, since, in consequence of the deplorable "Vivisection Act," this method of research is practically out of the reach of British chemists and physiologists. If the Society for the Advancement of Medicine by Research is still in existence, we would ask why it has never organised a laboratory, say at Calais, Boulogne, or Antwerp, where such experiments might be performed?

As regards the identification of the several poisons, the author gives some most useful precautions, and pieces of information which the expert may be suddenly called to produce. Thus, it was actually asked of a witness in the Tawell case, whether hydrocyanic acid might not have been introduced by eating apples. Now, Mr. Blyth mentions here that apple-pips contain 0.035 per cent of HCN! Attempts have in like manner been made to explain the presence of oxalic acid in the matter vomited by a patient and found in the stomach of a corpse by the hypothesis that the victim had been eating rhubarb pie or a salad containing sorrel.

A real difficulty arises in a case of nicotine poisoning if the deceased has been a heavy smoker or tobacco-chewer. How much nicotine may be introduced in this manner into a human subject it might be impossible to decide with any accuracy.

Under "Arsenic," we find a recapitulation of the salient points of the Maybrick case.

Want of space does not allow us to extend our notice of Mr. Wynter Blyth's work, but we may decidedly recommend it to every professional man who has not already familiarised himself with its contents.

Cambridge Natural Science Manuals. Physical Series. General Editor, R. T. GLAZEBROOK, M.A., F.R.S., Assistant Director of the Cavendish Laboratory, Fellow of Trinity College, Cambridge. *Solution and Electrolysis.* By WILLIAM CECIL DAMPIER WHETHAM, M.A., Fellow of Trinity College, Cambridge. Cambridge: The University Press. 1895. Pp. 296.

As a clear compact exposition of solution and electrolysis as now understood this little work will be found very valuable to students of physics and chemistry. After an account of the general properties of solution, the author goes on to describe the solutions of gases in gases, of liquids in gases, and of solids in gases.

In the third chapter the author proceeds to consider solutions in liquids, and solubility, showing the solubility of gases in liquids; the measure of solubility; Henry's law, the solutions of gases in saline solutions; the solubility of liquid and of solids in liquids; the influence of pressure and of temperature; the analogy between solution and evaporation; the solubility of mixtures, and solubilities of mixed liquids; followed by a Table of Solubilities.

In the fourth chapter we have an account of the principles of diffusion and dialysis. Mr. Whetham then proceeds to treat of the freezing-points of solutions, the determination of molecular weight, of cryohydrates, and of the melting-points of alloys.

The vapour pressures of solutions are discussed in the sixth chapter, after which, in the seventh, eighth, and ninth chapters, the author enters upon the electrical properties of solutions. Here the reader meets with an account of the ions, their migrations and velocities, the theory of dissociation, and electrical endosmose.

In the tenth chapter is shown the connection between electrical and other properties, such as chemical activity and osmotic pressure.

In the concluding chapter we find the theories of electrolysis, an interesting account of the colours of saline solutions, the general case of chemical equilibrium.

There is an appendix on freezing-points and a table of the electro-chemical properties of aqueous solutions.

The work will be found accessible to a wider circle of minds than might have been at first sight expected.

"Sanitas." *How to Disinfect.* A Guide to Practical Disinfection during Cases of Infectious Illness, and in Every-day Life. London: The Sanitas Company, Limited.

THIS pamphlet may be considered as essentially an abridgment of Mr. Kingzett's "Nature's Hygiene"—a work which we have had much pleasure in examining. The author adduces testimonies in favour of the Sanitas preparations from the most varied authorities, from eminent physicians and surgeons down to sporting characters and dog-fanciers. He declares war against the dictum that every disinfectant, to be efficacious, must be poisonous. He contends that the "Sanitas" preparations are of the highest value, not merely in combating cholera, yellow fever, diphtheria, &c., but in destroying or banishing aphides and other scourges of our gardens or orchards, though he makes no mention of their success or failure in the treatment of the phylloxera. The Sanitas oil is recommended for banishing mosquitoes or other analogous pests. We should like to ask Mr. Kingzett whether he has ever made a comparative trial with the extract of Marsh-rosemary (*Ledum palustre*), which has done such good service against mosquitoes and sand-flies (e.g., *Simulium columbianense*) in every climate where it has been tried.

It must be remarked that the Sanitas Company, Limited, do not confine themselves to the manufacture of the preparations patented under the name of "Sanitas." They are manufacturers of, and dealers in, hydrogen peroxide, a mercuric bactericide, corrosive sublimate pellets, and sulphur fumigating candles, and even of carbolic acid, of chlorides of lime and zinc, the permanganates, and of iron and copper sulphates.

For disinfectants, indeed, the field is still large, if we may judge from the recent prevalence of epidemics.

CORRESPONDENCE.

[DISINFECTANTS.]

To the Editor of the Chemical News.

SIR,—The remark with which Dr. Rideal seems dissatisfied was applied to the words which he quotes in his letter. He cannot, of course, deny that sewage contains phosphates, precipitable by salts of iron, aluminium, &c. He must admit that his words, "to recover the phosphate by using the sludge as a fertiliser," were open to the construction which I placed upon them, as referring to the total phosphates in the sewage sludge of what origin soever, and he is of course well aware that valuable quantities of phosphates may be found in sludges to which neither animal charcoal nor mineral phosphates have been added. Animal charcoal is now rarely, if ever, used in the treatment of sewage.

Utterly disclaiming any intention to disparage Dr. Rideal's work, I am, &c.,

YOUR REVIEWER.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxi., No. 7, August 12, 1895.

Special Microscope for the Observation of Opaque Bodies.—Ch. Fremont.—The author, after pointing out the defects of previous devices, e.g., that of Lieberkühn, describes his invention, which consists in illuminating the interior of the tube of the microscope through the object-glasses. The arrangement cannot be described intelligibly without the accompanying figure. The arrangement is said to afford a vertical illumination, very intense and perfectly defined, and to be especially adapted for microphotography.

Potassium Derivatives of Quinone and Hydroquinone.—Ch. Astre.—The author has studied the action of potassium upon quinone in ethereal or benzenic solutions and upon hydroquinone in a benzenic solution. The author, in concert with M. Ville, purposes extending his observations to other metals.

No. 8, August 19, 1895.

On Matches with Explosive Compositions.—T. Schloësing.—The author's results impress upon us the necessity of avoiding accidental ignitions during the operations after drying. We may indeed proscribise pastes of antimony and lead, although their compounds figure in all the pastes whether ancient or of recent invention, but we cannot proscribise phosphorus, and if this body reduces the fumes of its acid in the workshops we lose—at least in part—the essential advantage of the suppression

of white phosphorus. Hence the substitution of explosive pastes for pastes with white phosphorus is not so simple a matter as we may be tempted to believe.

Researches on the Compounds of Mercury Cyanide with Chlorides.—Raoul Varet.—Mercury cyanide, when acting on metallic chlorides, forms compounds of the type $2\text{HgCy}_2\text{M}^+\text{Cl}_2 \cdot n\text{H}_2\text{O}$. The author has made a thermo-chemical study of the mercury and sodium chlorocyanide, the corresponding compounds of mercury and ammonium, mercury and barium, mercury and strontium, mercury and calcium, mercury and magnesium, mercury and zinc, and mercury and cadmium.

Thermic Researches on Cyanuric Acid.—Paul Lemoult.—A thermo-chemical study, not suitable for abstraction.

Combustion-Heat of Certain β -Ketonic Ethers.—J. Guinchant.—Not suitable for abstraction.

Determination of the Heat Liberated in Alcoholic Fermentation.—A. Bouffard.—The heat liberated is between 24 and 32 cal. We must not calculate in the construction of refrigerators upon 71 cal.

On the Gum of Wines.—G. Nivière and A. Hubert.—The authors, in opposition to Pasteur and Béchamp, show that there exists a marked difference between the gum of wines and gum-arabic. The latter, when oxidised with nitric acid, only yields 35 per cent of mucic acid, whilst the gum of wine yields 70 to 75 per cent. If we boil the gum of wine with dilute sulphuric acid it yields no arabinose, but it is transformed into galactose, whilst reductive agents change it into dulcitol. Gum-arabic, if heated with dilute sulphuric acid, yields arabinose, and with reductive agents it forms arabitol.

No. 9, August 26, 1895.

Heat of the Solution and of the Formation of Sodium and Potassium Cyanurates.—Paul Lemoult.—The author's studies do not reveal any essential difference between the sodium and potassium salts. They show, further, that these salts are not decomposed by water.

On Apiculated Fermentation, and on the Influence of Aération in Elliptical Fermentations at High Temperatures.—M. Rietsch and M. Henselin.—The refrigeration of musts below 30° has more decided effects than aération. The combination of these two agencies gives the best practical results; this combination is the more indicated the more concentrated are the musts.

Utensils of Aluminium.—M. Balland.—The author's investigations have been undertaken with reference to military uses, for which the low specific gravity of aluminium is especially suitable. In the ordinary conditions of a soldier's life aluminium utensils offer a sufficient resistance to wear and friction, to the action of foods and of potable liquids. The metal takes a clouded appearance, but its weight after four months' use does not vary appreciably. Their contact with foods, &c., is of brief duration. On prolonged contact the action is more considerable. The behaviour of impure samples of aluminium—containing, as sometimes occurs, as much as 8 per cent of foreign matter—cannot be inferred from the author's experiments. Aluminium vessels should never be cleansed with soda, and solderings should be avoided as much as possible.

No. 10, September 2, 1895.

Presence of Argon and Helium in Certain Mineral Waters.—Dr. Ch. Bouchard.—(See p. 152).

Combination of Magnesium with Argon and Helium.—(See p. 153).

Researches on the Compounds of Mercury Cyanide with the Bromides.—Raoul Varet.—The author has continued his researches on the combinations of mercury cyanide with the bromides of the alkaline and alkaline-earth metals, of zinc and cadmium. The re-

sults, thermo-chemical data, do not admit of useful abridgment. At ordinary temperatures the solutions of the bromo-cyanides, mixed with the picrate of the same bases, yield, in course of time, traces of an isopurpurate. Mercury cyanide does not act upon tincture of litmus. On the contrary, the cyanides of the alkaline and alkaline-earth metals turn the red tincture to a blue. The solutions of the bromo-cyanides, contrary to the chloro-cyanides, turn litmus slightly blue even in the cold.

Formation of Hydrogen Selenide.—H. Péladon.—This paper requires the accompanying diagram.

Action of Carbonic Acid, of Water, and of Alkalies upon Cyanuric Acid and its Dissolved Sodium and Potassium Salts.—Paul Lemoult.—This paper, essentially thermo-chemical, does not admit of useful abstraction.

The Eclipsoscope, an Apparatus for observing the Chromosphere and the Solar Protuberances.—Ch. v. Zenger.—The description of this instrument should be accompanied by diagrams.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. x., No. 113.

Report presented by M. Jordan on behalf of the Committee of the Chemical Arts on F. Osmond's Paper entitled "A General Method for the Micrographic Analysis of Carbon Steels."—The method in question was in the first place due to Dr. H. C. Sorby, of Sheffield, who in 1864 laid before the British Association micro-photographs of various sorts of steel and iron, and elaborated a process for the study of the sections of the metals as preferable to fractures. Prof. Maters, of Berlin, in 1878, seems to have independently taken up the same line of research. MM. Osmond and Werth, of Creusot, further developed microscopic metallography. The former, in a paper here inserted, summarises the results hitherto obtained, and gives an account of the procedure to be adopted. In polishing the sections the author was induced to make use of liquorice-water in conjunction with jewellers' rouge and precipitated calcium sulphate, and found that it coloured certain constituents, leaving others untouched. After the polishing the action is continued by means of acids, halogens, principally nitric acid and tincture of iodine. The characteristics of iron and steels, with their peculiar constituents, ferrite, martensite, troostite, cementite, and sorbite, are shown in an illustration.

Report presented by M. Jordan on behalf of the Committee of Chemical Arts on the Researches of Mr. Hadfield on the Alloys of Iron with Silicon, Aluminium, and Chrome.—Mr. Hadfield's researches on chrome-steels are pointed out as of exceptional practical importance.

No. 114.

Elimination of Foreign Metals during the Production of "Best Selected" Copper.—Allan Gibb.—From the *Institute of Mechanical Engineers*.

Preparation and Properties of Pure Melted Molybdenum.—Henri Moissan.—The substance of this paper has already been noticed in connection with the *Comptes Rendus*.

No. 115.

The meeting of June 28th, 1895, was taken up with a notice of the prizes awarded for various inventions. Very few of these interest the chemist. F. Osmond obtained a prize of 2000 francs for a study of the physical properties of alloys in common use, especially steels. Jules Garçon obtained a prize of 500 francs for an account of the machinery employed in bleaching and dyeing textile fibres. The prize for the purification of potable waters, amounting to 2500 francs, has been divided

among four candidates—MM. Tellier, Lacroix, Schlumberger, and Meignen. Tellier proposes to sterilise water by the combined action of heat and pressure. Lacroix decomposes water by the electric current, liberating hydrogen, and generating ozone and "electrolytic oxygen." Schlumberger passes the water over pumice saturated with aluminium benzoate, and then over charcoal coated with manganese peroxide; this double filtration is said to destroy the greater part of the organic matter and almost all the bacteria. The process of Meignen is not described.

Communication by C. Bardy on the Process for Treating Crude Turpentine.—Gabriel Col.—The advantages of this process depend entirely on the structure of the plant employed.

The Determination of Small Quantities of Arsenic.—Ad. Carnot.—Noticed under the *Comptes Rendus*.

Reduction of Silica by Coke.—H. Moissan.—Also noticed under *Comptes Rendus*.

MISCELLANEOUS.

Special Manures.—Messrs. W. H. and L. Collingridge have just published a book on "Special Manures for Garden Crops," by Dr. A. B. Griffiths, F.R.S.E., F.C.S. The work contains about eighty analyses of plant-ashes (which represent over eighteen hundred separate weighings), performed by the author and his pupils. The work is quite unique and original.

Serpent Venoms.—According to Professor T. D. Fraser (*Transactions of the Royal Society of Edinburgh*), the venom of the cobra is sixteen times more powerful than that of the rattle-snake (*Crotalus horridus*). The "diamantine snake" of South Australia—a species not sufficiently identified—is intensely virulent, as of its venom 0.0015 grm. is equivalent to 0.004 grm. of rattle-snake poison.

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THE CHEMICAL NEWS.

VOL. LXXII., No. 1871.

ACTION OF NITRIC ACID ON CERTAIN SALTS.*

By H. A. AUDEN, B.Sc., and G. J. FOWLER, M.Sc.

THE experiments here recorded are part of a systematic investigation into the conditions of stability of the oxides of nitrogen. They are by no means complete, but the results so far obtained appear to be of sufficient interest to warrant a preliminary notice.

The reactions of nitric oxide have so far alone been studied. The gas was prepared by Emrich's method, viz., the interaction of sodium nitrite, strong sulphuric acid, and mercury. The mixture was kept in continual agitation by a specially contrived stirrer worked by a turbine. In this way a regular stream of gas is obtained, which analysis showed to be of a high degree of purity.

In order to study the action of nitric oxide upon the salts selected, a weighed amount of the salt was placed in a boat contained in a Lothar Meyer constant temperature furnace. By means of a thermostat, also devised by Lothar Meyer, the temperature can be kept to within one degree. Temperatures above the range of an ordinary instrument were measured by means of a high temperature thermometer, constructed by Max Kaehler and Martini, of Berlin, which would give accurate readings to over 400°. The salt was heated gradually in a stream of nitric oxide and the phenomena noted as the temperature rose; the salt was weighed at different intervals of temperature, so that it was possible to tell at what temperature reaction began, and at what point it attained a maximum velocity.

So far, oxy-salts have been chiefly studied. It was thought that by comparing their behaviour under the above conditions some light might be thrown on their stability and thence on their constitution. One or two oxides were fixed examined, the results agreeing with those of Sabatier and Senderens, *e.g.*, PbO_2 forms a basic nitrate of lead when heated in nitric oxide; the action begins at a temperature as low as 15°, but does not attain its maximum till over 130°.

MnO_2 behaves similarly, but the change is not so rapid as in the case of PbO_2 , probably owing to the smaller stability of manganese nitrate. The change is most rapid at 216°. In neither case with a peroxide are any but traces of a nitrite formed.

Silver oxide, however, at any rate if at all moist, yields a mixture of almost equivalent parts of silver nitrite and metallic silver at the ordinary temperature. At higher temperatures, with the dry oxide, nitrate and metallic silver are formed almost entirely.

Silver permanganate begins to be attacked at the ordinary temperature, and at 80° the alteration is very rapid. On analysis of the residue it was found to consist of metallic silver, silver oxide, silver nitrate, and manganese dioxide. Very little, if any, manganese nitrate was formed.

Potassium permanganate is much more stable than the silver salt. It is not appreciably attacked till over 100°, and the increase in weight becomes rapid at 190°. The residue on moistening was not alkaline, and no manganese could be dissolved out. The potassium is converted into nitrate and the manganese into oxide.

Interesting differences were noted in the behaviour of

other silver and potassium salts, notably the chlorates and iodates.

Potassium chlorate is attacked by nitric oxide at the ordinary temperature, chlorine being evolved in considerable quantity, and nitric peroxide being formed. The gaseous product was condensed in a tube immersed in a freezing mixture, and the percentage of chlorine in the brown liquid obtained was determined. It was found to be much in defect of that required to form nitrosyl or nitroxyl chloride, so that the reaction does not consist simply in the formation of an oxy-chloride of nitrogen. On analysis of the residue in the boat no chloride of potassium was found to be present. Nitrate was formed, and also a slight trace of perchlorate. This seems to be direct proof that in potassium chlorate the potassium and chlorine are separate.

With barium chlorate a similar reaction took place.

With silver chlorate (prepared according to Stas's method), chlorine was given off, but a considerable amount of silver chloride was also formed—nearly one-third of the silver present being found as chloride. This may be due to a difference in constitution between the chlorates of silver and of potassium, or to a difference in stability of the products of reaction. That some difference of constitution exists between the silver and potassium salts appears to derive confirmation from the behaviour of their iodates when treated with nitric oxide.

Potassium iodate, heated to 80° in nitric oxide, begins to give off iodine, and the reaction becomes rapid at 110°, crystals of iodine condensing on the cool portion of the tube. No trace of iodide, however, is formed, as is shown by there being no liberation of iodine on acidifying a solution of the residue after adding some potassium iodate. The residue is not alkaline, the potassium being converted into nitrate, recognised by the evolution of ammonia when the residue is warmed with zinc-dust and caustic soda.

Silver iodate, on the other hand, is stable up to a rather higher temperature than the potassium salt, and when heated above this temperature, about 110°, no trace of iodine is given off, but all the silver is converted into iodide, none being dissolved out by water, and the yellow residue being insoluble in dilute nitric acid.

The perchlorates and periodates which have been examined show themselves more stable than the corresponding chlorates and iodates.

Potassium perchlorate does not begin to be attacked till above 200°. A small quantity of chloride was found in the residue, but the high temperature (over 300°) employed may have induced secondary changes. The potassium for the most part is converted into nitrate, there being considerable loss of chlorine.

Barium periodate is stable up to 200°, when iodine is given off. On heating to 388° much iodine is given off, and barium iodide found in the residue.

Of the salts so far examined, chromates have shown themselves the most stable, being analogous in this respect to the sulphates.

Lead chromate was unaltered at a temperature exceeding 400°.

Silver chromate did not suffer appreciable change till above 300°. Metallic silver was found to be present in the residue as well as silver nitrate. The chromium was all converted into the sesquioxide. Some amount of nitrite of silver was also formed. Silver sulphate is only slightly attacked at the highest temperature of the furnace.

It was found in certain cases, *e.g.*, with lead nitrate, that the intermixture of a decomposable oxide, *e.g.*, PbO_2 or MnO_2 with the salt caused the latter to be attacked at a temperature below that at which action begins with either the salt or oxide taken separately.

Experiments have also been in progress on the interaction of nitric oxide and various gases, but the results are not yet quite complete enough for publication.

* Read before the British Association (Section B), Ipswich Meeting, 1895.

THE FORMATION AND PROPERTIES OF A
NEW ORGANIC ACID.*

By HENRY J. HORSTMAN FENTON, M.A

WHEN tartaric acid is oxidised under certain conditions in presence of a ferrous salt a substance is produced which acts as a powerful reducing agent, and which gives a beautiful violet colour with ferric salts in presence of alkali. This substance has after considerable difficulty been isolated, and proves to be a dibasic acid having the formula $C_4H_4O_6.2H_2O$.

The constitution of this acid is now under investigation.

Heated with hydrogen iodide it gives succinic acid, racemic acid being an intermediate product. Bromine in presence of water oxidises it quantitatively to dioxy-tartaric acid. Heated with water it is resolved into carbon dioxide and glycollic aldehyd.

This aldehyd has been obtained as a viscid liquid, pure except for a trace of ether; and, on removing the latter by heating in a vacuum, the aldehyd undergoes polymerisation, a sweet-tasting solid gum being the result. Analysis and molecular weight determinations show that this gummy substance has the formula $C_6H_{12}O_6$ (*Journ. Chem. Soc.*, 1894, 899; 1895, 48 and 774).

Further observations have recently been made as to the conditions under which this new acid may be obtained from tartaric acid. The presence of a ferrous salt is essential. Ferric, manganous, and various other salts have been tried with negative results.

If moist ferrous tartrate be exposed to the air for a short time a certain quantity of the new acid is produced, and may be indicated by the characteristic violet colour given when caustic alkali is added. The effect is much more intense if the exposure be made out of doors, and the increased result was at first attributed to some constituent of the fresh air (e.g., hydrogen dioxide; ozone seems to be inoperative). But later experiments show conclusively that light is the cause. Air which has been purified by passing through potassium iodide and caustic potash solutions gives an effect about equal in intensity to that produced by fresh external air, if the exposure to light is the same in both cases. That oxygen (or some oxidising agent) is essential is shown by the fact that exposure in a vacuum, even to bright sunlight, gives a negative result.

DATA FOR THE ASCERTAINMENT OF THE
TRUE ATOMIC WEIGHT OF CARBON.

By J. ALFRED WANKLYN.

IN December, 1893, I wrote in the *Philosophical Magazine*:

"An investigation which has occupied me for the greater part of the year has yielded the following result. There is a series of hydrocarbons the successive members of which rise in molecular weight—not by $CH_2=14$ —but by $\frac{1}{2}(CH_2)=7$. If this result cannot be overturned, the consequence follows that the atomic weight of carbon is 6."

The series concerning which I wrote at the close of the year 1893 was the hydrocarbons existing in Russian kerosene imported into this country. That series would, according to the prevailing knowledge of the day, be termed a series which was only imperfectly understood. Continuing our work, my colleague Cooper and myself have recently published (*Philosophical Magazine*, August, 1895) a parallel investigation with a parallel result, given by a series of hydrocarbons which the knowledge of the day pronounces to be comparatively well explored

and well understood. The series is the marsh gas series, which is now regarded as the backbone of organic chemistry.

The paper published last month in the *Philosophical Magazine* contains a concise statement of our work, and we proceed to quote from it as follows:—

The first term of the marsh gas series which figures in our table is the fifteenth member of that series. In an admirable paper of Schorlemmer's, published in the *Journal of the Chemical Society* for the year 1863, a liquid is described under the name of hydride of heptyl, which we believe contained at least 50 per cent of our marsh xv. (formula $C_{13}H_{17}$). Quoting from that paper we find that a combustion of the liquid gave 83.93 per cent of carbon, 16.13 per cent of hydrogen, and the determination of vapour density 3.59, which is a figure between that required for hydride of heptyl and our marsh xv., and which indeed approaches nearer to that required by marsh xv. than to the figures required by hydride of heptyl.

The figures are theoretical V.D. of marsh xv. = 3.697; theoretical V.D. of heptyl hydride 3.455. Obviously therefore the figures obtained by Schorlemmer, 3.59, agrees better with our view than with that held by himself thirty years ago.

As I hold that the only datum given in Schorlemmer's paper which is valid as a piece of evidence capable of deciding between the two formulæ is the V.D. determination, I hope I may be pardoned for going over Schorlemmer's calculation, the correctness of which I am able to confirm. I make, however, this note, there is no mention made of the size of the inevitable air-bubble in the Dumas-determination, and if we suppose that this air-bubble was of the usual size when the workmanship is excellent (as Schorlemmer's workmanship always was), the correction for the air-bubble would bring Schorlemmer's figures very close to marsh xv.

A consideration of all the circumstances of the case leads me indeed to the belief that Schorlemmer's hydride of heptyl of the year 1863 consisted mainly of marsh xv., mixed with hydride of heptyl.

The main body of Schorlemmer's paper, which I am at present quoting, is occupied with an account of the chlorination of the hydrocarbon and the various derivatives of one of the products of the chlorination. It is an admirable piece of chemical workmanship, and deserves proper appreciation.

There are two classes of reaction in organic chemistry, viz., the complete and the incomplete.

Chlorination of such a body as marsh xv., or heptyl hydride, is notoriously an incomplete reaction. This fact becomes very apparent in Schorlemmer's account of the operation. It is impossible to take a quantity of the hydrocarbon and transform the whole of it, or anything like the whole of it, into a monochloride. Only a portion of the hydrocarbon undergoes chlorination in this operation and the "unattacked hydride," as Schorlemmer says, was distilled off after the termination of the chlorination. The monochloride was then separated by fractional distillation from the accompanying di-chloride, and from the still more highly chlorinated products which are the inevitable companions of the mono-chloride as yielded by the process of chlorinating a hydrocarbon. The mono-chloride (which is described as a liquid boiling at 150°) does not appear to have been submitted to analysis, but was employed in the preparation of the acetic ether by reaction upon acetate of potash. Great difficulty was experienced in pushing the reaction to completeness, and, furthermore, only a portion of the monochloride underwent transformation into the acetic ether. The olefine heptylene as well as acetate of heptyl are described by Schorlemmer as arising from the reaction upon acetate of potash.

The acetate of heptyl described by Schorlemmer was therefore derived from the original hydrocarbon by two incomplete reactions, and is not a fair representative of

* Read before the British Association (Section B), Ipswich Meeting, 1895.

the whole of the original hydrocarbon. The acetate was analysed and its analysis agreed with the formula for acetate of heptyl. It was also converted into the corresponding alcohol by a process which is known to be complete when applied to the acetate. The alcohol was also converted in a thoroughly satisfactory manner into the iodide, and both alcohol and iodide were analysed with good results, the iodide especially being beautifully in agreement with the theory. When these results are fairly considered they indicate the probability that some portion of the original hydrocarbon consisted of heptyl-hydride, but they afford no ground for the conclusion that the whole or even the greater proportion of it consisted of that hydride. There is a curious piece of evidence pointing in the other direction. The olefine (which accompanies the acetate of heptyl) was investigated. It was sealed up with hydriodic acid and heated to the boiling point of water for twelve hours and converted into an iodine compound, which on analysis was found to contain only 55.73 per cent of iodine instead of 56.19 required by the iodide of the heptyl series.

The circumstance that the other iodide gave almost exactly the theoretical result, viz., 56.18 per cent of iodine, lends importance to this discrepancy, which Schorlemmer does not in any way explain.

A by no means unlikely explanation of the discrepancy is that the iodine compound was a mixture of the derivative from our marsh xv. with the derivative from hexyl-hydride.

In criticising this work of Schorlemmer's nothing is further from my intention than to belittle it. A very important general fact is established by it and by the researches of Cahours and Pelouze and Carius. That fact is, that one atom of hydrogen in the marsh gas series of hydrocarbons is replaceable by chlorine, which in its turn suffers replacement by other radicals so as to yield the alcohol, the mercaptan and the various ethers. Until, however, the chlorination process has been much improved it cannot be valid as a method of distinguishing between heptyl-hydride and the fifteenth term of the marsh gas series.

In due time we expect to exhibit the intermediate alcohols and their various derivatives, but at present we have no intention of taking in hand this branch of the investigation. We are at present engaged with the physical side of the subject, and with only such chemical changes as do not involve the destruction of the hydrocarbons.

Inasmuch as the process by which we have been able to separate the hydrocarbons from one another is fractional distillation, we have applied ourselves to the task of measuring the vapour-tension of the individual hydrocarbons at different temperatures.

Every chemist knows that the every day operation of taking the boiling point of a liquid is in point of fact a special vapour-tension observation, and that the boiling point is another name for that point of temperature at which the tension of the vapour of the liquid is equal to 760 m.m. of mercury, the average pressure of the atmosphere. Instead, therefore, of using a distillatory apparatus and observing the temperature registered by the thermometer immersed in the vapour of the liquid during distillation, we might arrive at the same result by the employment of the apparatus for measuring the tension of the vapours evolved by liquids at different temperatures.

The apparatus which we employ we have ourselves constructed, and one of its peculiar advantages is that by its aid we are able to ascertain the boiling point of a very minute quantity of liquid. A single decigramme of a specimen of liquid is amply sufficient for such determinations.

Our work in this direction is only just at the commencement, and this map of vapour tensions is a preliminary chart (a chart accompanies the paper), exhibit-

ing part of the curve of tension of eleven consecutive terms of the kerosé series.

The *Tensio-meter* (as we name our new instrument) has a future rich in promises. In carrying out the fractionation of a mixture of liquids boiling very near together, it provides a criterion indicative of the completion of the fractionating process. When the distillation has been pushed to complete dryness there will always be a few drops of residual liquid on allowing the retort to cool. When the tension of those few drops approximates to the tension of the original liquid—that is a sign that the fractionation has reached completeness, and the *Tensio-meter* enables that comparison to be made.

Light on the question whether, in a given instance, there is specific adhesion between the constituents of a mixture may be looked for by having recourse to this instrument, which imparts a degree of certainty and completeness to the fundamental operation of fractional distillation which has hitherto been altogether wanting.

In conclusion I exhibit four terms of the marsh gas series, viz.:—

Marsh xi.	formula	$C_{11}H_{23}$
Marsh xv.	"	$C_{15}H_{31}$
Marsh xvi.	"	$C_{16}H_{33}$
Marsh xvii.	"	$C_{17}H_{35}$

In presence of these substances chemists will be compelled to revert to that atomic weight of carbon which was all but universally admitted forty years ago.

Laboratory, New Malden, Surrey.

ON THE FORMATION OF CITRIC ACID BY THE OXIDATION OF CANE-SUGAR.

By EDWIN F. HICKS.

SOME time ago Dr. Phipson, in the *CHEMICAL NEWS* (vol. lxxi., p. 296) announced that he had obtained an acid which he regarded as citric acid, as a result of the oxidation in the cold of an acidulated (H_2SO_4) solution of cane-sugar with permanganic acid. After the solution became clear, it was carefully neutralised with ammonia, calcium chloride solution was added, and the solution on boiling gave the precipitate which was described as containing citric acid.

Soon after this announcement, Messrs. Searle and Tankard repeated Dr. Phipson's work with great care (*CHEMICAL NEWS*, lxxii., 31), and although they obtained a precipitate on neutralising, adding calcium chloride and boiling, it did not in any way resemble calcium citrate. On the contrary, this precipitate was proved, by analysis and microscopical examination, to consist in every case of hydrated calcium sulphate, $CaSO_4 \cdot 2H_2O$. Further, when nitric acid was used for the acidulation in place of sulphuric, no precipitate was obtained on treating and boiling the solution as before.

Previously to the work of Searle and Tankard I had done some few experiments according to the directions given in Phipson's note. Owing to lack of time my results obtained then were not conclusive as to the nature of the precipitate, except that I could not confirm it as being calcium citrate according to any of the ordinary tests for citric acid.

Recently, having more time at my disposal, I again undertook to repeat the experiments, following out the directions given by Dr. Phipson as exactly as possible, but varying the conditions in order to note any difference in the course of the reaction with different relative amounts of acid and permanganate, as well as the concentration of the solution. My results in every way corroborate those anticipated by me in the work of Searle and Tankard.

The results of my experiments may be briefly sum-

marised. When the solution contains a greater quantity of H_2SO_4 than 1 to 100, precipitation takes place on standing in the cold; and for equal concentration and permanganate added, is greater the more acid present. On filtering and boiling further precipitation takes place.

When the amount of acid present is less than 1 to 100, no precipitation takes place in the cold, but on boiling a finely crystalline white precipitate is formed, its relative amount bearing the same relation to the amount of acid present as in the first case. On adding alcohol to the filtrates from these precipitates a further precipitate is thrown down. All the precipitates obtained were thoroughly washed with boiling water.

One description will suffice for all, whether obtained by precipitation in the cold, after boiling, or on treating the filtrates with alcohol. In every case they consisted entirely of pure hydrated calcium sulphate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. No trace of any organic acid was found. All the precipitates were finely crystallised and easily identified with the microscope, which was supplemented by obtaining the confirmative chemical tests.

I also used a nitric acid solution and obtained results identical with those described by Searle and Tankard (*loc. cit.*).

In conclusion, it would seem that this work, although largely a repetition, is not altogether out of place, as Dr. Phipson in a second note (*CHEMICAL NEWS*, vol. lxxii., 100), not having repeated his experiments, seems to doubt the conclusions, and has pointed out certain possible errors of conditions in the work of the two chemists mentioned above.

I think my work has completely covered these conditions, and can leave no doubt as to the composition of the precipitate, and has further shown that it is obviously futile to look for the formation of citric acid, unless other conditions than those specified are admitted.

52, Beaver Street, New York City.
September 16, 1895.

ON THE VOLUMETRIC DETERMINATION OF METALS.

By M. LESCEUR.

L. BARTHE has recently given a process for determining the free acid and the metal in a salt of zinc containing acid in excess. To this end he uses a normal alkali and two indicators, phenolphthalein and the colouring matter of the red hollyhock. He ascribes to the precipitate formed by the alkaline solution in the salt of zinc at the moment when the phenolphthalein turns of a rose colour the composition of a basic salt, $(\text{ZnO})_2\text{SO}_4\text{Zn}$. Hence it is necessary to multiply the number of c.c. of the normal solution of potassa by $\frac{1}{2}$ in order to calculate the metal in the manner usual in volumetry.

For several years I have employed for the volumetric determination of metals in salts in presence of an excess of acid a method almost identical with that of Barthe. As an indicator I use simultaneously methyl-orange (Orange No. III. of Poirrier) and phenolphthalein. The former indicating by its gooseberry tint the presence of a free acid, and becoming decolourised by the addition of alkali at the exact moment when neutrality is reached; the second indicating the moment when free potassa exists in the mixture, and showing by its change the end of the precipitation. As for zinc, I have not observed the formation of a sub-salt. Analysis shows that the product collected at the moment of the change of colour of the phenolphthalein, after washing and desiccation, is zinc oxide. Perhaps the washings effected after precipitation have destroyed the basic salt?

The following experiment shows that this is not the case, and destroys the hypothesis of Barthe:—

One gram. of commercial zinc sulphate, titrated with

normal soda (caustic), required 6 c.c. of the solution to turn the colour of the phenolphthalein (a result corresponding only to 0.861 grm. of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$). The precipitate is collected upon a filter, washed with boiling water, and re-dissolved in hydrochloric acid. But on the one hand, the washings do not contain zinc, and on the other hand, the hydrochloric solution does not contain sulphuric acid.

The precipitate is therefore zinc oxide free from sulphate. The method is only rendered more simple, no correction being necessary, and the normal solutions of soda and zinc being volumetrically equivalent.—*Bull. de la Soc. Chim. de Paris.*

ON THE DETERMINATION OF BORIC ACID.

By H. JAY and M. DUPASQUIER.

AMONG all the procedures for determining boric acid, that with methylic acid is the most trustworthy, as it enables us to isolate with accuracy the total product to be determined. The modification which we have introduced into this method, which consists in the manner of distillation, and the peculiarity of the titration, enables us to apply it in all cases, which was not practicable with the operation as hitherto described.

The substance in question, dried and pulverised, after being freed from any organic matter, is acidulated with hydrochloric or sulphuric acid in very small excess, introduced, along with 25 to 30 c.c. of methylic alcohol, into a flask fitted with a cork having two perforations. One of these orifices admits a perpendicular tube bent at its lower end, descending almost to the bottom of the flask and traversing a refrigerator at its upper part. The other orifice admits a delivery-tube leading into a second flask, like the former, and plunging to the bottom. A second delivery-tube, sealed to the perpendicular tube, enters the second flask, which before the commencement of the operation receives 1, 2, or 3 c.c. of a normal solution of potassa or soda (freed from carbonic acid), according to the supposed quantity of boric acid, and having always an excess of alkali.

The two flasks, when connected, are heated separately in the water-bath. The methylic alcohol conveys the boric acid from the first flask to the second, in which it is retained by the alkalis, finding its way into the refrigerator to re-descend again, effecting in a continuous manner the complete extraction even of large proportions of the boric acid. The time consumed by the operation is variable, but for 300 m.-grms. it does not exceed ninety minutes.

After having experimented with various indicators, we prefer litmus paper and the blue C. L. B., the latter already indicated by Engel.

The alkaline liquid containing the boric acid is gently heated so as to expel the methylic alcohol and to be concentrated to a constant volume; it is then rendered slightly acid by means of a few drops of dilute hydrochloric acid, warmed afresh to volatilise any traces of carbonic acid which have been introduced during the distillation. We cool to 15–20°, and titrate with a decinormal solution of potassa or soda free from carbonic acid until a small drop placed upon litmus paper is found neutral. Then follows the titration of the boric acid. We add to the liquid two drops of an aqueous solution of blue C. L. B., at 10 grms. per litre, and pour anew the titrated liquid until the first change of tint. The quantity of liquid employed, after deducting 0.2 c.c. or 0.3 c.c., according to volume, indicates exactly the proportion of boric acid present.

The conditions necessary for obtaining exact results are uniform volumes and constant temperatures, as also the elimination of the carbonic acid and of methylic alcohol.

In a series of experiments on wines to which known quantities of boric acid had been added along with, in some cases, hydrochloric acid and fluorine compounds,

the authors found that hydrofluoric acid alone effected a slight excess of the proportion introduced, and falsified the results to that extent. But they believe that this slight excess may be neglected in practice. The process has been further verified upon wines of different growths, upon ciders, perries, and wines.—*Comptes Rendus*, cxxi., p. 260.

REPORT OF COMMITTEE ON ATOMIC WEIGHTS, PUBLISHED DURING 1894.*

By F. W. CLARKE.

(Continued from p. 157).

PALLADIUM.

In 1889 Keiser published his determinations of the atomic weight of palladium, for which, since then, other investigators have found somewhat different values. He has now, jointly with Mary B. Breed, given a new set of determinations, which confirm his former series (*Am. Chem. J.*, xvi., 20). As before, palladiumammonium chloride was reduced in hydrogen, the salt being prepared by two methods and carefully examined as to purity. Two series of experiments are given, with the following weights of material:—

First Series.		
Pd(NH ₄ Cl) ₂ .	Pd.	At. wt. Pd.
1'60842	0'80997	106'271
2'08295	1'04920	106'325
2'02440	1'01975	106'334
2'54810	1'28360	106'342
1'75505	0'88410	106'341
From sum of weights		.. 106'325
Reduced to vacuum		.. 106'246
Second Series.		
1'50275	0'75685	106'297
1'23672	0'62286	106'296
1'34470	0'67739	106'343
1'49059	0'75095	106'353
From sum of weights		.. 106'322
Reduced to vacuum		.. 106'245

The atomic weight was computed with H = 1, N = 14'01, and Cl = 35'37. If O = 16 this becomes Pd = 106'51. This is only 0'02 less than the value obtained in the earlier investigation.

TUNGSTEN.

A new determination of the atomic weight of tungsten, by Pennington and Smith (read before the American Philosophical Society, Nov. 2, 1894), leads to a much higher value than that commonly accepted. The older work seems very probably to have been done upon material contaminated with molybdenum, an impurity which was eliminated in this investigation by Debray's method,—that is, by volatilisation by means of gaseous hydrochloric acid. The metal, carefully purified, was oxidised in porcelain crucibles, with all necessary precautions, and the following data are given:—

Wt. W.	Wt. O ₂ .	At. wt. W.
0'862871	0'223952	184'942
0'650700	0'168900	184'923
0'597654	0'155143	184'909
0'666820	0'173103	184'902
0'428228	0'111168	184'900
0'671920	0'174406	184'925
0'590220	0'153193	184'933
0'568654	0'147588	184'943
1'080973	0'280600	184'913

Mean .. 184'921

All weights are reduced to a vacuum, and O = 16 is taken as the standard of reference.

Another paper, by Smith and Desi, was read at the same meeting with that just cited. In this research, the tungstic oxide was purified in the same way, and reduced by heating in a stream of pure hydrogen. The water formed was weighed, and all weights reduced to a vacuum. Computed with O = 16 and H = 1'008, the results are as follows:—

Wt. WO ₃ .	Wt. H ₂ O.	At. wt. W.
0'983024	0'22834	184'683
0'998424	0'23189	184'709
1'008074	0'23409	184'749
0'911974	0'21184	184'678
0'997974	0'23179	184'704
1'007024	0'23389	184'706

Mean .. 184'704

Why this result should be lower than that previously found by Pennington and Smith remains to be explained.

(To be continued).

ON THE VAPOUR-TENSIONS OF MIXTURES OF VOLATILE LIQUIDS.*

By C. E. LINEBARGER.

Introductory.

THE investigation of the elastic forces or tensions of vapours emitted by a solution of a fixed substance in a volatile liquid has received much attention, especially within recent years. The impetus for investigations of this kind is, in a great measure, due to the new notions that have been introduced into science in regard to the nature of solutions. The possibility of ascertaining the molecular mass of a substance from a determination of the amount of the depression of the vapour-tension of a liquid, occasioned by its being dissolved therein in known proportions, has induced chemists to study carefully this field of scientific inquiry, which it may truly be said has been gone over very elaborately.

In the greater part of the work that has been done, both theoretical and experimental, it has been assumed that the dissolved substance is not appreciably present in the gaseous state, and but sparingly present in the liquid state; in other words, the dissolved substance is supposed to be involatile, and the solutions are made dilute.

Now, absolute involatility in any body whatsoever cannot be affirmed; there must always be, at every temperature, some degree of power of assuming the gaseous state, although it may be so slight as to be imperceptible to our senses. Still, for all practical purposes, the assumption of non-volatility in many substances can be admitted, as our means of experimentation are not sufficiently delicate to detect any small amount of volatility.

Although so much has been done on the vapour-tensions of solutions of fixed substances in volatile liquids, comparatively little attention has been paid to the study of the vapour-tensions of mixtures of the volatile liquids; yet this is the general case, of which the restriction that the dissolved substance be fixed makes only a special application. It must, indeed, be allowed that the consideration of a mixture of vapours, instead of a single one, introduces certain complications into the problem; and this is, perhaps, just the reason so little work has been done on this part of the subject; still difficulties of this sort are probably not unsurmountable.

The limitations of work on vapour-tensions to dilute or, at most, moderately concentrated solutions cannot be

* From the *Journal of the American Chemical Society*, vol. xvii., No. 3. Read at the Boston Meeting, Dec. 28, 1894.

* Abridged from the *Journal of the American Chemical Society*, vol. xviii., No. 8, August, 1895.

said to be satisfactory. True, the theory of solutions has been developed on the hypotheses that dissolved matter, in analogy with gaseous matter, is in a state of considerable dilution; and experimental confirmations of theoretical predictions can be expected only when such a state of affairs is realised. Notwithstanding that circumstance, it seems of importance to extend our line of operations and attack the problems presented by concentrated solutions; perhaps they will be found to exhibit fewer anomalies than has been supposed.

There are two circumstances which render work that has hitherto been done on the vapour tensions of mixtures of volatile liquids of all concentrations unsatisfactory; they are to be found in the choice of the liquids investigated, and the kinds of vapour-tension measured. The liquids chosen were almost invariably those which are now recognised to be made up of associated molecules; they are just those which exhibit the greatest abnormalities in respect to most of their properties, and it cannot be expected that simple relations, if they exist at all, will be discovered when such liquids are used as material of investigation. All investigators also, almost without exception, have measured only the total pressure of the mixtures of liquids examined, which is the sum of the partial pressures, these, however, being entirely unknown. But more important is it to know the share which each vapour has in the exerting of the total pressure, and only when this is learned can our knowledge of the matter be said to be in any adequate measure complete.

This paper seeks to fill in some degree this gap in the subject of vapour-tensions. The method employed is such as to permit of the specification of the partial pressures of a mixture's components, and also of their concentrations in the gaseous phase. The choice of the liquids has been made with an eye towards employing those which have been found to be most "normal," so that in the examination of more complex liquids, that is, those consisting of associated molecules, the simplicity to be expected in the phenomena of the former may aid us in getting some light on the possible intricacies of the latter. All the mixtures examined are freely soluble in one another, so that no disturbing influence from layer-formation can take place.

In reality, we have before us a case of equilibrium; the equilibrating system consists of two substances, each present in two phases, the liquid and gaseous. We have to ascertain at the points of equilibrium the temperature, the partial pressures of the two substances in gaseous phase, and their concentration in both liquid and gaseous phase.

Description of Apparatus.

It is of prime importance in the determination of vapour-tensions that the temperature be kept uniform; accordingly I describe, first of all, the apparatus employed for that purpose.

Thermostat.—This consisted of a cylindrical copper vessel holding nearly forty litres of water. It was heated by means of a ring burner; the pressure of the gas was kept constant by means of a pressure-regulator, and a thermo-regulator as described by Ostwald (*Ztschr. Phys. Chem.*, ii., 565, 1888), controlled by combustion of the gas. To insure uniformity of temperature in all parts of the bath, the water was kept in constant agitation by means of a number of fine streams of air blown up through it, the laboratory being provided with air under pressure. Such a means of agitation gives very satisfactory results; it takes up but very little room, and permits of the examination of the pieces of apparatus plunged in the water by shutting off for a few seconds the flow of the air.

The temperature of the bath remained constant to within 0.05° during an experiment; the thermometer employed was one graduated to tenths of degrees, and had recently been tested by the "Physikalische Reichsanstalt" of Berlin.

The apparatus consisted of three principal parts, each made up from material easily found in almost every chemical laboratory. The first part consists of those pieces required to measure a definite volume of air, to compress it enough to force it through the apparatus, and to dry it thoroughly; the second part is the contrivance for saturating the volume of air with the vapour of the liquid under examination; and the third is the arrangement for the analysis of the gaseous mixture.

First Principal Part of Apparatus.—This consists of a measuring vessel, a vessel for regulating the internal pressure, a manometer, and a system of drying tubes. I pass to the description of each.

The Measuring Vessel consists of an ordinary bottle of a capacity varying from one to three litres, according as it is required to employ a larger or a smaller volume of air; the height of the bottle should be such that only the neck is above the water; in its neck is fitted a good rubber stopper through which passes one branch of a T tube. This branch of the T tube is made of tubing of about a quarter inch bore, and is about eight inches long, while the other branch has only half this bore, with a length of about 3 inches. The wider branch of the tube is pushed through the stopper so that its lower edge is just flush with that of the rubber, and care is taken that this adjustment is in every experiment maintained, as well as that the stopper is always inserted to the same distance in the neck of the measuring vessel. In the upper end of the wider branch of the T tube is inserted (an air-tight joint being assured by the use of rubber tubing) a tube somewhat drawn out and narrowed at its lower end, and provided with a stop-cock at its upper end. The end of the lower part must be about a half inch above level of the stop of the measuring vessel, and the upper end is put, by means of a piece of rubber tubing, in communication with a water supply at constant level about a yard above the thermostat. If the stop-cock be opened water will flow into the vessel, and displace the air therein contained which escapes through the side branch, which, being in the middle of the vertical branch, is an inch or so above the orifice of the tube introducing the water.

Sufficient mercury is poured into the vessel to make it sit firmly on the floor of the thermostat. The residual volume of the vessel is carefully determined by pouring into it from graduated vessels, enough water to fill it up to the level with the upper surface of the stopper. If the adjustment of the stopper and the tubes be always the same, duplicate determinations of the capacity do not differ by more than one-half c.c. If the same volume of mercury always be taken, the volume of water will represent the volume of air passed through a liquid or mixture of liquids undergoing investigation in all determinations.

It is superfluous to make corrections for the expansion of the mercury and the glass when determinations of vapour-tensions are made at higher temperatures, as the error of the estimation of the capacity exceeds the amount of the corrections.

The Pressure Regulator consists of a bottle of any convenient size, provided with enough mercury to make it stand steadily under water, and fitted with a twice perforated rubber stopper. Through one of the holes of the stopper passes a tube nearly to the level of the mercury and furnished with a stopcock at its upper end; this tube is connected by means of rubber tubing with the same water source as the measuring vessel. In the other hole is fitted a T-tube, of which one of the horizontal branches is connected by means of a bit of stout rubber with the narrower branch of the T-tube belonging to the measuring vessel, while the other is attached by rubber tubing to the other parts of the apparatus. If water be run into the bottle serving as pressure regulator, the air in it is compressed until it can force itself through the liquid with the vapour of which it is to be saturated.

The Manometer is intended to measure the amount of this compression or the internal pressure; it is made of ordinary glass tubing bent into U-shape, with the branches

about two feet long. It may be put between the measuring vessel and the pressure regulator, or between the drying tubes and the latter; I have found it most convenient, however, to melt it into the vertical branch of the T-tube of the measuring vessel just opposite the horizontal branch, as shown in Fig. 1. The manometric liquid is water, and the differences of the heights of the liquid columns of the two branches, is read to a millimetre by means of a metric rule; the readings are then easily exact to a tenth m.m. of mercury.

The Drying Tubes can, of course, be of various shapes and filled with various drying agents. Liquids, such as strong sulphuric acid, must be rejected, however, as they increase the internal pressure, and often cause an irregularity in the flow of the gas. I found U-tubes to be the best shape, and grains of pumice stone, soaked in concentrated sulphuric acid, the best drying agent; a length of at least 60 c.m. is to be taken, and the pumice must

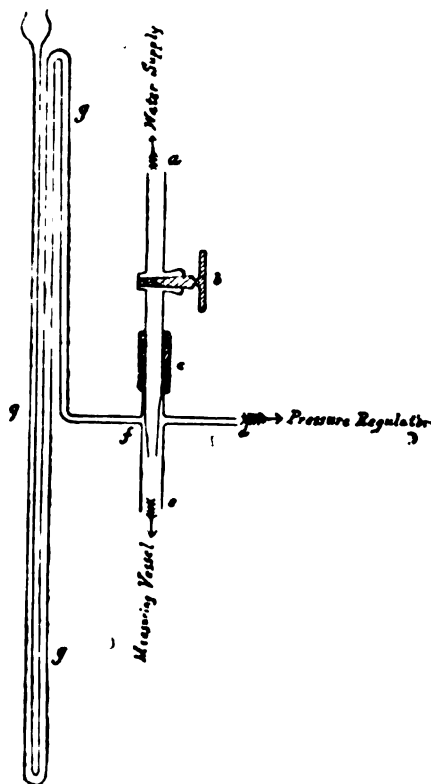


FIG. 1.

be changed often. When it becomes necessary, in work on acid solutions, to remove the carbon dioxide from the air, an additional tube filled with soda-lime is taken. At the end of the last U tube, a mercury valve is attached to prevent the backward diffusion of the vapours; this is of the smallest size convenient, and the delivery-tube dipping into the mercury of capillary dimensions.

Second Principal Part of Apparatus.—This is the absorption vessel, which may consist of a simple potash bulb according to Mohr. I found it better, however, to add two more bulbs, making five small and two large ones. As liquids which dissolve rubber somewhat were often introduced into the apparatus, and as it was necessary to let it stand some time before weighing, the outlet and inlet tubes were provided with tiny ground glass stoppers. At first the bulbs were shut up in a copper case set in the thermostat; the case had holes in its sides, below the surface of the water, for the conduction and

abduction of air, platinum capillaries and ground glass caps being employed to make the connections. This arrangement was not, however, found satisfactory, since one was never sure, air being such a bad conductor of heat, that the contents of the bulbs had the same temperature as that of the bath. Also, the platinum tubes proved to be very delicate, breaking readily if bent often, which was inevitable. It was accordingly found best to plunge the absorption vessel directly into the water of the bath, connection with the system of drying tubes being made with a bit of stout rubber tubing of small bore. When the vessel was removed from the water it was carefully wiped dry and set in the balance case, the atmosphere of which was kept dry by means of concentrated sulphuric acid.

Third Principal Part of Apparatus.—In order to analyse the mixture of vapour issuing from the absorption vessel two modifications of this part of the apparatus are required—one to be employed when the gaseous mixture contains a halogen compound of carbon, and the other when it contains an acid. In the first, the compound was decomposed by heated lime, and, in the second, the acid was absorbed by a solution of potash or baryta. In the following lines a description of each is given.

1. The outlet tube of the absorption apparatus is fitted by means of a good cork into one branch of a U-tube of rather thick glass; this branch is bent at right angles at about the middle of its length, while the other branch is left straight. The latter branch is held clamped to a heavy, and hence steady, retort-stand set beside the thermostat, and is connected by means of a narrow lead tube to a tube of hard glass placed in the gutter of a combustion furnace. In the further end of the hard glass tube, a Maquenne absorption apparatus, containing a little dilute nitric acid, is inserted, the connection being made with a rubber stopper; this outlet of the absorption apparatus is in communication with a suction pump, and in the rubber tube making this connection a T-tube is interposed, over the open end of which is slipped a piece of rubber tubing long enough to reach to the thermostat. When this tube is open, the interior of the apparatus, up to the liquid in the absorption vessel, is under atmospheric pressure; if it be pinched together a little so as to prevent enough air to feed the suction pump from entering, the pressure in the apparatus may be made less than that of the atmosphere; by this little device it is possible to regulate the pressure with great nicety.

2. This analysing apparatus consists simply of a potash bulb, according to Liebig, made of thick glass; one branch is flared out to receive the outlet tube of the absorption vessel, and the other is straight so as to glide up and down in a clamp of a retort-stand.

The pieces of apparatus just mentioned will receive complementary description in the directions for performing experiments.

Performance of an Experiment when the Mixture contains an Organic Halogen or Sulphur Compound.—The hard glass tube (about 80 c.m. long) is filled with lime or sodium carbonate just as in a determination of halogens in organic analysis, joined to the lead tubing which establishes communication with the U-tubes held in a clamp just above the surface of the water in the thermostat, and placed in the furnace. The gas is now lighted and the tube with its contents heated up to a red heat, while a current of dried air is passed through it to remove all moisture.

The measuring vessel, the pressure regulator, and the system of drying tubes are joined air-tight together, and so set in the thermostat that as much room as possible is left for the absorption vessel.

The absorption vessel is filled with the liquid or solution under examination, a few bubbles of air drawn through so as to get the liquid beforehand in the right position, and carefully weighed. It is then connected with the U-tube (of course, no air is now being passed through the analysing tube), and after a couple of

minutes of half-submersion in the bath, it is attached to the system of drying-tubes. It is now wholly submerged in the bath and air is made to pass through it as follows:—

The stopcock of the pressure-bottle is opened so that water may be run in slowly and, by compression of the air, gradually increase the internal pressure. As soon as bubbles of air commence to pass out of the absorption vessel, the stopcock of the pressure-regulator is closed, and that of the measuring vessel opened. The water issues in drops or a fine stream in full sight of the operator, and its rapidity of flow can be very easily regulated. Experience has taught me that about a litre an hour was about the best rate; after a brief acquaintance with the apparatus, it is possible to judge very closely from the rate of the flow how long it will take for the measuring vessel to become filled. While the operation is proceeding, the height of the manometric column is read off at several different times; if the rate of flow is constant this does not vary by more than 1 or 2 m.m. of water, or less than one-tenth m.m. of mercury.

The barometer is also read off at the beginning and at the end of the experiment; in all my determinations, the difference of the two readings was less than one m.m. of mercury.

A minute or so before the measuring vessel is full, the absorption-bulbs are lifted out of the water enough to bring the end-tubes about 2 inches above the surface, and there, together with the joining tube on one side and the cork and end of U-tube on the other, are carefully dried with filter-paper. When the water in the measuring flask has reached the mark on the T-tube (level of cork), the absorption vessel is detached from the drying-tubes, and the little glass stopper fitted into its inlet tube. Immediately after this operation the connection between the absorption vessel and the U-tube is broken, and as soon as this is done a perforated cork, through which passes a narrow glass tube so bent at right angles that a long vertical branch is obtained, is fitted into the U-tube, its object being to prevent the escape by diffusion of any portion of vapour contained in the U-tube. A current of air is now drawn through the tubes, slow at first to avoid causing too much vapour to pass over upon the heated lime all at once, as, if there be a deficit of air, the combustion is incomplete, and free carbon collects in the cooler portion of the tubes; in a well-conducted experiment, the lime should remain perfectly white. Towards the end of the determination, a more rapid stream of air is drawn through the apparatus, so that one may be sure that all the halogen compound has been brought into contact in the decomposing agent. If any free carbon collects in the tube, or if the dilute nitric acid in the Maquenne absorption-bulb shows on the addition of silver nitrate the slightest trace of cloudiness, the determination ought to be rejected as untrustworthy.

The absorption vessel, as soon as possible after its removal from the water in the thermostat, should be closed with the second tiny stopper, wiped dry, and set in the balance case, where it takes on the temperature of the room. When this is thought to have taken place, it is weighed, and the loss of weight set down as the evaporated quantity of solution. When the furnace has cooled down the lime tube is removed, and its contents washed out with water and nitric acid into a flask, which is set over a flame and boiled until complete solution ensues, more nitric acid being added if necessary. If more than a half grm. of the halogen compound has evaporated, the solution is brought to a certain volume and an aliquot portion of it taken for analysis.

Most of the analyses were made by the gravimetric method of determination of halogens by precipitation with silver nitrate; some, also, were analysed volumetrically, Volhard's method being employed.

Performance of an Experiment when the Mixture contains an Acid.—The absorption vessel is filled with the mixture being investigated, and weighed as described

above. It is then joined by means of a good cork to the analysing apparatus, into which are run from a pipette 10 c.c. of a stock solution of potash or baryta; the pipette being provided with a straight calcium chloride tube filled with soda-lime, all contamination from the carbonic acid of the breath is avoided. The alkaline liquor is of such strength that it is more than sufficient to neutralise the vapourised acid. The further end of the analysing arrangement is closed with a U-tube filled with soda-lime, so that the alkaline solution may be in contact with an atmosphere free from carbon dioxide.

The two pieces of apparatus thus filled and joined together are submerged in the water of the thermostat, the whole being held in place with a clamp embracing the upright tube of the analysing contrivance and attached to a heavy retort stand. The other end of the absorption vessel is then placed in communication with the drying tubes, &c., by means of a short bit of stout rubber tubing.

The internal pressure is regulated and the air passed just as described in the preceding section, note being taken of the amount of internal pressure, the volume of the air, and the barometric height. A slight correction has to be made to the barometric reading for the following reason:—After the air passes the liquid contained in the absorption vessel, and comes into the analysing tube, it is under a pressure equal to that of the atmosphere plus that due to the weight of a column of liquid corresponding to the difference of level between the two surfaces of the alkaline solution; this, in my apparatus, was determined to be equal to 1 m.m. of mercury, which was added to all barometric readings.

When the measured volume of air has passed through the apparatus, the stopcock, through which water enters into the measuring vessel, is closed, the absorption and analysing vessels are lifted nearly out of water, and after the joint between the absorption vessel and the system of drying tubes has been wiped dry, it is broken. Both the pieces of apparatus are wiped dry with bibulous paper, and agitated somewhat so that any acid vapours in the bulbs may be brought in contact with and absorbed by the alkaline liquor.

The pieces are then disconnected, the absorption vessel stoppered and set in the balance-case, while the contents of the analysing vessel are poured into a beaker, rinsing being done with water free from carbon dioxide. Without delay, the excess of alkali is estimated by titration against decinormal acid solution, and by a simple calculation the quantity of evaporated acid is obtained.

(To be continued).

OBITUARY.

THE LATE LOUIS PASTEUR.

ON September 29th Science, and especially the science of France, underwent a severe loss in the person of Louis Pasteur, one of the most successful students of that world of wonders, "the infinitely little." In our brief notice of the illustrious deceased we must first point out that he was not a medical practitioner, not even in the strict sense of the word a biologist. He was essentially a chemist—of course, in the French and German acceptance of the term. His earliest scientific studies and his first discoveries were on chemical questions. His scientific education was developed at the Ecole Normale, an institution which permits and even encourages individual effort. He observed for the first time the characteristic difference between tartaric and paratartronic acid, the crystals of the former having no plane of symmetry in common with those of the latter. He separated the double sodium and ammonium paratartrate into two salts having an inverse action on the plane of polarisation of light. The welcome which this capital discovery received from Biot

and other leading Academicians won for Pasteur the position of Assistant Professor of Chemistry at the University of Strasburg. His researches now led him to the conclusion that all the products of inorganic nature are not dissymmetrical, while vegetable and animal products are atomically dissymmetrical. In this characteristic he hoped to find the key to the problem of animating inorganic matter. He discovered a connection between the researches of chemistry and crystallographic physics, and the dawning results of physiological chemistry. His attention was now turned to the study of fermentation. He was nominated Dean of the Faculty of Sciences at Lille. As the district is largely interested in the manufacture of alcohol, he resolved to devote a course of lectures to the study of fermentation. He soon recognised the influence of the presence of a living organism. This view involved him in a controversy with Liebig, which ultimately terminated in the recognition of the new theory which was found applicable in the manufacture of vinegar. Liebig, it must be added, declined Pasteur's challenge to submit the question to an experimental investigation before an Academic Commission.

Next arose the question of spontaneous generation. Redi, Spallanzani, and Swammerdam denied the possibility of this alleged process. Aristotle, Buffon, and Pouchet affirmed it. It became the duty of Pasteur to take a decisive part in the contest. He had just been entrusted with the scientific studies at the Ecole Normale. But he had no laboratory, and had to furnish one at his own expense in a garret at the Ecole Normale! At last Pouchet and Joly, his opponents, withdrew from the contest. It must be remembered that the cause of spontaneous generation—heterogeny—suffered severely from the experiments of Tyndall.

The importance of Pasteur's researches has since been extending. They have thrown a new light on the manufacture of wine and beer, and on the propagation of disease, both in man and in the lower animals. At the present time we are on the point of recognising in a development of Pasteur's researches, a means of conferring on man immunity against malaria and against the bites of the most deadly serpents.

Surely we may pronounce the life-work of Louis Pasteur glorious, alike from the point of view of pure science, and that of practical utility; glorious to himself and to his country.

NOTICES OF BOOKS.

Die Genesis der Elemente von William Crookes. Ein Vortrag gehalten in der "Royal Institution" zu London, am 18ten Februar, 1887. ("The Genesis of the Elements, by William Crookes: a Discourse delivered at the Royal Institution of London, on February 18th, 1887.") Brunswick: Friedrich Vieweg and Son. 1895.

We have before us the second edition of the German version of Mr. Crookes's Discourse on the "Genesis of the Elements."

The translation is from the pen of Prof. Dr. W. Preyer, who is not merely a thorough English scholar, but whose researches have been to a considerable extent devoted to kindred subjects. Hence he has been able and willing to present to the German scientific public the views of Mr. Crookes not only *accurately* but *fairly*.

This double qualification is no mere tautology. Just as an orator can lead his hearers astray without ever being guilty of technical falsehood, so a writer in transferring profound scientific speculations into a foreign tongue may discredit them without laying himself open to the charge of inaccuracy. The author, without accepting the views of Mr. Crookes as a creed outside of which there is no salvation, admits that the picture which he has drawn of the development of the chemical ele-

ments is worthy of the highest attention. He considers that "whatever objection the physicist may take, there is, from a purely chemical point of view, in the chain of thought neither a chasm nor a sin against recognised facts." He tells us, in his Preface, that "there is probably no single living chemist who, *e.g.*, assumes that *e.g.* cerium and lanthanum have always existed in the quantity now present." It appears to him quite inadmissible that each of the several elements of the earth's crust must have existed at all times in exactly the present quantities. "Hence elementary mutations of matter must have occurred, or must still occur, in regions of the universe other than the small cold crust of our earth, mutations by which new elements have arisen and may arise from simpler materials."

We cannot, however, help pointing out that both Mr. Crookes in his original discourse (p. 2, line 3) and Prof. Preyer seem to assume—the former overtly and the latter by implication—that Prof. Mendeleeff recognises the evolutionary origin of the elements.

Prof. Preyer contends further, in his Preface, that even if the entire cosmogonic hypothesis of condensation, rendered probable by Kant and Laplace, is superseded by something preferable, the discourse of Mr. Crookes has—for the present at least—a special value, on account of his peculiar method of utilising the method of fractional precipitation and of spectral synthesis.

Prof. Preyer's preface will be valuable to German students as showing his exact position in reference to the views of Mr. Crookes, and to elemental evolution in general.

We find here, also, a series of appendices of great interest. In the first of these, concerning elements and meta-elements (see a Discourse delivered by Mr. Crookes at the Annual Meeting of the Chemical Society, March 28th, 1888), Prof. Preyer writes:—"A fact hitherto overlooked is in a remarkable connection with the hypothesis of Prout, resting as it does on a purely evolutionary foundation. The atomic weights of hydrogen and the seven elements of the first stage of condensation (hence the eldest and those of the simplest structure) come nearest to whole numbers (Li, G, Bo, C, N, O, F). In the elements of the second stage only four display this approximation; in those of the third stage only three; and in those of the fifth only two. Hence in the simpler elder elements the meta-elements play a quite subordinate part, but become more prominent in those formed subsequently, as the hypothesis of Crookes would demand."

A second appendix discusses the identical spectra of different substances. The identity of the spectra obtained by Crookes on a prolonged fractionated precipitation of the yttrium derivatives reminds him of the spectral identity of the hæmoglobines colouring the blood of all red-blooded animals. Prof. Preyer has found the absorption spectra of the red blood-pigment of certain insect larvae (*Chironomus*), of a mollusk (*Cardita sulcata*), and the common earthworm (*Lumbricus*), are identical with the red blood-crystals of vertebrate animals. Notwithstanding this universal agreement in a fundamental property, the hæmoglobines differ from each other physically and chemically. Their solubility, crystallisability, and their proportion of crystalline water differ. They crystallise in at least two systems. Their quantitative composition, their coagulability, their liability to decompose, differ according to the species. If species have been modified in the course of long eras, the hæmoglobines—though fulfilling all the conditions of a true chemical compound—must have become modified step by step with the species (in a morphological sense). Hence we see that the conception of evolution must necessarily find a place in chemistry, not merely as regards the elements, but as regards the formation of highly complicated though crystalline compounds.

The scheme of the pedigree of the elements is expounded and illustrated in a third appendix.

A fourth appendix relates to Radiant Matter and the

Phosphoroscope, as displayed by Mr. Crookes at the Meeting of the British Association held at Sheffield, on August 22nd, 1879.

The Organic Elements form the subject of a fifth appendix. Hence Prof. Preyer raises the question why only the organic elements, H, C, N, O, F, Na, Mg, Si, P, S, Cl, K, Ca, and Fe, in the living vegetal and animal tissue, can keep up the vital process. He refers to the treatise "On Chemism in Living Protoplasm," by himself and Wendt (See *Himmel und Erde* for October 1st, 1891; Berlin, Hermann Pretel).

The last appendix treats of Argon and Helium. Prof. Preyer thinks the assumption that argon is a modification of nitrogen not more improbable than that of its discoverers, who regard it as a totally new element. But he holds that there are no such objections to the elementary character of helium. In conclusion, he remarks that the main difference between our present systematic chemistry, on the one hand, and our present systematic natural history on the other, in comparison with the former chemistry and natural history, is that we were formerly content with artificial, *i. e.*, arbitrary systems, whilst in our present systems we have to regard not merely that which now exists, but that from which it has been evolved. Such systems are not arbitrary, but natural, since they follow the course of Nature: they are genetic.

Polytechnic Institute of Brooklyn. The Course in Practical Chemistry.

THIS prospectus gives an account of the equipment and organisation of the Brooklyn Polytechnic. Foremost stands a body called the "Corporation"—equivalent, we presume, to the *Senatus Academicus* in German seats of learning. Next comes the "Faculty," in which chemistry is not too copiously represented. There is only one Professor of the science, the widely-known Dr. P. T. Austen. The two "Instructors" in quantitative and qualitative analysis, and the assistants in chemistry, take apparently a lower rank. Some departments seem, on the contrary, to be over-represented. Thus we find a professorship of history and philosophy, a principal of the academic department, a professorship of ancient languages, a professorship of physical science and engineering, besides another of applied mathematics and engineering, and one of physics and electrical engineering. Doubts may arise as to the respective boundaries of these departments.

In the studies of the Chemical Course we find some—as it seems to us—superfluous matter, such as logic, moral philosophy, rhetoric, debates, perspective. We fear that such an introduction of extraneous matter will infringe upon the time and the brain-power needed for Science. We are glad to see that, in the laboratory work of the Chemical Course, spectrum analysis is not omitted. Nothing is said about microscopy and microbiology.

There is an illustration showing a corner of the library, the chemical lecture-room, the laboratory for qualitative analysis, in which the students have their faces all turned in one direction, and of the laboratory for qualitative analysis.

We have full confidence in the efficiency of Prof. Austen as the head of a chemical college, but we fear his hands will not be quite free.

Programme of the Royal Technical High School at Aix-la-Chapelle for the Year of Studies 1895—1896. ("Program der Königlichen Technischen Hochschule zu Aachen.") Opening October 1st and ending July 31st, 1896. Aix-la-Chapelle: C. H. Georgi.

THIS eminent Polytechnic School continues to prosper. The number of students for 1894—1895 was 259 as against 236 in the previous year. The divisions are—I. Architecture; II. Constructive Engineering; III. Mechanical Engineering; IV. Mining and Metallurgy,

Chemistry, and Electro-chemistry; V. General Sciences, especially Mathematics and Natural Sciences.

In Faculty IV. the professorial staff includes Dr. Andreas Arzruni (mineralogy and petrography), Dr. Ludwig Claisen (organic chemistry), Dr. Classen (inorganic chemistry and electro-chemistry), F. Dürre (metallurgy and assaying), Dr. Holzapfel (palæontology and geology), and Dr. Stalschmidt (technical chemistry). In addition there are two *doctes* and ten assistants.

In Faculty VI. we find that H. Storp gives instruction in industrial hygiene, Dr. W. Müller in first assistance in sudden accidents, and Anton Lieven, M.D., gives a course of practical bacteriology.

The school has a mineralogical institute, comprising a museum and laboratory; a laboratory for analytical and inorganic chemistry, including electro-chemistry; a laboratory for organic chemistry; a museum of chemical preparations; a laboratory for technical chemistry; a physical museum and laboratory; and a botanical institute.

The full course of study in each faculty extends over four years. The lectures and the practical work in botany are compulsory only for "food-chemists."

During the autumn recess (August and September) there take place excursions to mines, metallurgical and chemical work, conducted by professors of the departments concerned. No expert can examine this prospectus without being impressed with the complete and thorough-going character of the courses of instruction given at Aachen. It may even be questioned whether the courses of study prescribed are not in some cases so comprehensive as to sin against the principle of the division of labour.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxi., No. 11, September 9, 1895.

Nitro-Substitutions.—C. Matignon and M. Deligny.—The authors give a comparative table of the combustion-heats with those of the substances in which substitution is effected, and they propose the law that the isomers of position have the same combustion-heat, excepting errors of experiment. It is therefore sufficient in these thermic studies to operate upon a single one only of the three terms, the ortho, meta, or para. The differences oscillate around 4.5 cal., and are sensibly constant.

Explosion of Endothermic Gases.—L. Maquenne.—Not suitable for useful abstraction.

No. 12, September 16, 1895.

Researches on the Phosphates of Algeria. Case of a Phosphatic Rock of Bougie presenting the Composition of a Superphosphate.—H. and A. Malbot.—The authors have made a comparative study of several phosphates from the Department of Constantine, some of which are remarkable for their richness in phosphoric acid, such as those of Bordj-bou-Arreidj, and others for their friability, which renders them fit for immediate utilisation as plant food. The phosphatic rock of Bougie is extremely interesting, as containing phosphoric acid in three different conditions. The white portion contains 13.29 per cent of phosphoric anhydride soluble in water, 8.51 per cent insoluble in water but soluble in ammonium citrate, and 11.70 per cent insoluble in water and in ammonium citrate; in all 33.50 per cent of phosphoric anhydride. The red portion of the rock contains 2.03 per cent of phosphoric anhydride soluble in water,

and 12.39 per cent soluble in ammonium citrate. The white or exterior portion, after desiccation in the stove, loses 27.42 per cent at dull redness. Unless this is done, there is an error in deficiency if the phosphoric acid is determined by precipitation as magnesium-ammonium phosphate in a citric solution, as compared with the result obtained by precipitation as ammonium phosphomolybdate. After ignition at a red heat the two methods agree absolutely.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xiii.-xiv., No. 8, 1895.

Crystalline Compound of Ferrous Chloride with Nitric Oxide.—V. Thomas.

Ammoniacal Salts of Silver.—A. Reyckler.—The author gives a table showing the results of his cryoscopic experiments on these salts, proving that the addition of 2 mols. ammonia per equiv. of silver or copper scarcely at all modifies the molecular lowering of the congelation-point. He adds theoretical considerations on the constitution of the ammoniacal silver salts.

Action of Formic Aldehyd upon the Amines and on their Salts.—R. Cambier and A. Brochet.

Hexachlorobenzene Parabichloride.—Et. Barral.—The decomposition of carbon chloride, C_6Cl_8 , by heat or by the majority of reagents into hexachlorobenzene and chlorine, $C_6Cl_8 = C_6Cl_6 + Cl_2$, shows that it is an addition product of hexachlorobenzene, in which the position of the two Cl is given by (1) its transformation into tetrachloroquinone under the influence of oxidising agents; (2) its preparation by means of tetrachloroquinone and phosphorus pentachloride.

Constitution of a-Hexachlorophenol and of Quinone.—Et. Barral.—The author shows that the formula of Fittig gives the constitution of quinone, and that it is a diketone, possibly of a peculiar kind.

Basic Properties of the Rosanilines and their Sulphonic Derivatives. A Reply to M. Prudhomme.—A. Rosenstiehl.—The author explains the formulæ which he has assigned to acid magenta and to sulphonic rosaniline. He shows what he has said in his former publications of the basic functions of the rosanilines, and he lastly examines whether the magentas should be regarded as ethers or as salts.

Are the Magentas Ethers or Salts?—A. Rosenstiehl.—There exists in the derivatives of triphenylmethane an assemblage of compounds in which the alcoholic function varies in a continuous manner between two extremes, as in the mineral oxides the acid function and the basic function vary, though it is not easy to draw a boundary. To unite the formulæ of an ether and to call it a salt is to collide against a word.

Analysis of the Gastric Juice.—J. Winter.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xxx., No. 3.

Rapid Determination of Phosphorus in Steels.—The most practical procedure consists in transforming the phosphorus into phosphoric acid, precipitating it with molybdic reagent, and determining the apparent volume of the precipitate after having effected its rapid settlement and its regular heaping up by means of centrifugal force. This method, proposed by Eggertz in 1860, was not at first appreciated as it deserved, but since 1887 it has been studied and improved, and is now in regular use. Various authors describe methods of operating slightly different. Von Jüptner proceeds as follows:—He weighs out, for medium proportions, 2 grms. of the sample (more for low percentages, and less for highly phosphidic steels), dissolves in 30 c.c. of nitric acid (sp. gr. 1.2), completes the oxidation by means of permanganate, and then causes the manganic precipitate to disappear by means of a

small quantity of oxalic acid. To the solution is added 0.75 gm. of ammonium nitrate, the mixture is heated to 60°, and treated with 50 c.c. of the molybdic solution. The temperature is kept at 60° until the precipitation is completed, and then left to settle until the liquid is perfectly clear. The liquid is decanted, and the precipitate is washed into a special vessel by means of a washing-bottle charged with ammonium nitrate. The receiving vessel is contracted at its lower part and terminates in a narrow tube graduated in cubic millimetres in which the precipitate is collected. The graduated vessels, thus charged, are introduced into a small turbine, which is set in motion at the rate of 1000 rotations per minute, a speed which is kept up for four minutes. After stopping the rotation, the volume of the precipitate is read off on the graduated tube. If the surface of the precipitate is not perpendicular to the axis of the graduated tube, we read the level of the lower part and that of the upper part and take the mean. To find the proportion of phosphoric acid in the steel assayed from the volume of the precipitate, Ledebur gives the figure of 0.0025 per cent per cubic millimetre, when operating on 0.882 gm. of steel, which is equivalent to 0.0022 per cent if we operate upon 1 gm., or 0.0011 for 2 grms.

Zeitschrift für Analytische Chemie.
Vol. xxxiv., Part 3, 1895.

Contributions to the Analysis of Must and of Wine.—A. Halenke and W. Moslinger.—This paper is too voluminous for insertion.

Contributions to the Isolation, Quantitative Separation, and Chemical Diagnosis of Alkaloids and Glykosidous Substances in Forensic Cases, with especial reference to their Detection in Putrescent Human Bodies.—Dr. Kippenberger.—This memoir also does not admit of abstraction.

New Process for the Determination of Indigotin.—Josef Schneider (*Casopis pro Průmysl Chemický*, 1893).

Remarks on the Sweet Wines of Austria-Hungary.—Leonhard Roesler.—A memoir not calculated to interest our readers. We mention merely the fact that more than half of the samples of Tokay and analogous wines contain per litre more than 0.55 gm. of phosphoric acid.

Determination of Sulphur and Chlorine by means of Sodium Peroxide.—A. Edinger.

New Method of Separating Copper and Cadmium in Qualitative Analysis.—Allerton S. Cushman.—Already inserted.

Analysis of the Nitrogenous Components occurring in Meat Extracts and in Commercial Peptones.—A. Stutzer.

Detection and Determination of Metals in Fatty Oils.—H. Fresenius and A. Schattenfroh.

MISCELLANEOUS.

City and Guilds of London Institute.—At the recent Matriculation Examination of the City and Guilds Central Technical College, 76 candidates presented themselves, and 62 have been admitted to the College. The highest place was taken by M. Solomon, to whom the Clothworkers' Scholarship of £60 a year and free education has been awarded.

Spontaneous Combustion of Wool.—It is not sufficiently known that wool, if packed in bales whilst in a damp state, is, like cotton, liable to what is called spontaneous combustion. The action is not as violent in wool as in the case of vegetable fibre, and it has never yet been known to spread to other kinds of goods in the same ship or warehouse. But wool sometimes arrives in England scorched, and seriously deteriorated in value.

Steam-Boiler Explosions.—During the year 1894 no fewer than 35 such calamities occurred in Germany. The number of the sufferers was 34, of whom 12 were killed, 9 severely wounded, and 13 slightly injured. The most frequent causes are said to have been insufficient supply of water and local weakness of the plates from age.—*Chemiker Zeitung*.

New Poisons.—The Cape *Agricultural Journal* is calling attention to a poison not yet fully understood. It is obtained from *Acocanthera venenata* (or *Toxicophlaea Thunbergii*), known to the colonists as Gift-boom or Poison-tree. The leaves have proved rapidly destructive to many goats, and a decoction of the bark of the root is used medicinally by the native quacks, sometimes with fatal effect. In one case, where the medicine was administered as an enema, death ensued in about two minutes. It is conjectured that the active principle is not an alkaloid, but a glucoside. No analysis of the poison has been published, nor have its reactions been studied. The arrow-poison used by the Bushmen is said to be prepared by mixing the venom of the African cobra with the gum-resin which exudes from the rhizomatous base of the "gift-boll," *Brunsvigia toxicaria*. Whether the latter ingredient has any effect beyond preventing the cobra poison from being rubbed off the point of the arrow has yet to be ascertained.

Max Dreverhoff's Filter-papers.—We have received from Max Dreverhoff, of Dresden, a price-list and a number of samples of excellent filter-papers. No pains appear to have been spared to produce papers to meet the requirements of all departments of chemistry. M. Dreverhoff has succeeded very well in the great aim of all manufacturers of filters, to produce a paper that will allow liquids to pass rapidly and at the same time retain very fine precipitates. We notice the special filters that have been treated with HCl and HF: these appear to be quite strong, and a 9 c.m. circular paper on incineration leaves only 0.00006 grm. of ash. Filters of this quality, at the very reasonable prices at which they are offered, will prove a great boon to the chemist. We also note the ready-folded filters as being neatly made, and not unreasonable in price. M. Dreverhoff's price-list is very complete, giving minute particulars of all his manufactures, and, for the greater convenience of foreign customers, some of the more important announcements are given also in French and English; but in this latter endeavour the writer has unfortunately got a little mixed—for after various slips in the body of the list, he gravely expresses a belief that "the filters must satisfy the highest pretensions of the most painful analytical chemist." We trust they will prove of better quality than the English.

A New Safety Paraffin Lamp.—We are glad to find that manufacturers are becoming alive to the dangers that accompany the majority of cheap paraffin lamps, and, taking warning from the terrible accidents that are too frequently recorded, especially in the houses of the working classes, are bringing to the front lamps that are within the reach of all, and are at the same time designed upon true principles with a view to reducing, as far as possible, the risk of accident accompanying their use. In this direction the little lamp that has been sent to us by Messrs. Kiesow and Co. is a happy example. The reservoir is made entirely of metal, furnished with two convenient handles (the value of which is often overlooked); the burner, instead of fitting into the oil-chamber with the usual loose screw, has a simple and efficient bayonet fitting. An ingeniously devised S-shaped tube, attached to the burner, carries the wick down into the body of the reservoir, diminishing to a great extent the danger of the oil escaping in case of the lamp getting overturned. On the whole we consider the lamp to be a good step in the right direction, and hope it will meet with the appreciation it deserves.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Assaying.—Can any of your readers tell me of any book suitable for the practical assaying of such things as brass ashes, zinc ashes, type ashes, tin ashes, &c.? I have "Berlingier," but he does not treat of these.—S. J. HASEWOOD.

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The Council does not bind itself to accept the lowest or any tender, and it will not accept the tender of any person or firm who shall on any previous occasion have withdrawn a tender after the same has been opened, unless the reasons for the withdrawal were satisfactory to the Council.

H. DE LA HOOKE, Clerk of the Council.

Spring Gardens, S.W.,
27th September, 1895.

THE CHEMICAL NEWS.

VOL. LXXII., No. 1872.

THE ACTION OF LIGHT UPON THE SOLUBLE METALLIC IODIDES IN PRESENCE OF CELLULOSE.*

By DOUGLAS J. P. BERRIDGE, B.A., Malvern College.

THE action of light upon the metallic iodides appears not to have been thoroughly investigated by any chemist, and, although it has frequently been taken for granted by some experimenters that potassium iodide suffers decomposition when exposed to sunlight, others have passed the subject over in silence, and, so far as I am aware, no text-book upon chemistry mentions the fact. The experiments, an account of which I have to-day to lay before the Section, were commenced in the year 1884, and it was not until eight years later, during most of which interval I had been prevented from finishing my work, that I heard of Videau's investigations; in 1892 I came across a notice of them in Prof. Meldola's book, "The Chemistry of Photography," but as, by a reference to the original paper, I found that Videau had worked upon an altogether different principle from my own, and his results left much to be cleared up, I have continued to prosecute my experiments. Last year a paper was read before the Chemical Society, by Dr. Cook, upon the effect of heat upon iodates and bromates, in the course of which he mentions (*J. Chem. Soc.*, 1894, p. 804) that ordinary purified potassium iodide "liberates iodine when exposed to air and light," but that if the iodide be previously purified by crystallisation from absolute alcohol no such decomposition takes place. Dr. Cook does not mention in his paper the precautions he took to prevent the access of carbon dioxide from the air to his solution, which was contained in a test-tube, and as impurities would be probably more abundant in the open air than in a dark cupboard it seemed to me, after reading his paper, that a more satisfactory method of experiment would be to seal the solution of the iodide in a bulb with a known quantity of air, thus preventing any CO₂ from reaching the liquid and disturbing the results. I may, however, say at once that after doing this my experiments fully confirm Dr. Cook's. Solutions of the so-called pure salt, which, when tested with starch and tartaric acid, gave no immediate colouration, were always decomposed when exposed in sealed tubes containing air to the sunlight; the amount of iodine liberated, however, varied considerably; on the other hand, a solution made with potassium iodide which had been previously fixed with charcoal gave no colouration upon the addition of starch, even after an exposure to sunlight for several weeks.

It is, however, to the decomposition of the iodide in presence of cellulose that I more especially wish to call your attention; in the earlier experiments my method was to saturate a sheet of paper with a solution of the desired iodide, and to expose this to the sunlight in a printing frame under a negative; in my later experiments I have, however, confined myself to the use of sealed bulbs, since by this method only can any quantitative results be obtained. I at first experienced a certain amount of difficulty in obtaining a form of cellulose suited for the purpose, and many experiments in which cotton-wool was used failed, owing to the presence of sodium thiosulphate in the material, from which it could only be removed with great difficulty. When, however, I substituted filter-paper which had been extracted by hydrochloric acid

hydrofluoric acids for the cotton-wool, much more satisfactory results were obtained. The paper used was that supplied by Schleicher and Schüll, and was in all cases tested for acid, from which it was, however, perfectly free; after reducing a certain quantity of this paper to pulp, and well washing with distilled water, it was introduced into a bulb; the solution of potassium iodide, generally containing a known weight of the salt, was added, and the bulb sealed. After exposure to sunlight the bulbs were opened, a little starch added, and the amount of iodine liberated determined by a centinormal solution of thiosulphate of sodium.

In a typical experiment 85.724 grms. of potassium iodide were dissolved in 500 c.c. of distilled water and five sheets of the pure filter-paper, 12.5 c.m., treated as described, were introduced into a bulb of about 100 c.c. capacity and 50 c.c. of the iodide solution added. In another bulb, of the same size, 50 c.c. of the solution were sealed without the addition of pulp. After an exposure of about four hours to diffused sunlight, the former had acquired a decided reddish colour, whilst the latter remained perfectly colourless; at the end of twenty-five days, during which the bulbs had been exposed in a window, they were opened, when 0.001778 grm. of iodine was found to have been liberated in the former, whilst in the latter only 0.000635 grm. of free iodine was found.

When a solution of half the above strength was used, i.e., one containing 4.286 grms. of potassium iodide dissolved in 50 c.c. of distilled water, the influence of the cellulose was even more marked, for in the bulb containing 50 c.c. of solution and five sheets of extracted paper 0.001524 grm. of free iodine was found, whilst in one containing the same quantity of solution but no pulp, only 0.000091 grm. of iodine had been liberated. In a fifth bulb the same quantity of paper pulp was placed, and the solution of potassium iodide was poured off after the pulp had become thoroughly soaked with it. In this case the liberation of iodine occurred much sooner than in the previous cases, but considerably less was liberated during an exposure of five and twenty days, the total being only 0.000762 grm. The contents of all these five bulbs were tested for alkali with a solution of phenolphthalein; the two in which there was no pulp gave decided colouration with this reagent, whilst the three containing cellulose proved to be quite free from alkali.

In another series of experiments a stronger solution of potassium iodide was used, viz., one containing 76.936 grms. of the salt dissolved in 250 c.c. of water, and this was sealed in bulbs containing a varying quantity of the paper pulp. Four bulbs were taken; in the first, half a sheet of paper reduced to pulp was placed, in the second one sheet, in the third two sheets, and in the fourth four sheets; 40 c.c. of a solution of the strength above described, and therefore containing 12.308 grms. of the salt, were added. These were exposed in a window for ten days, at the end of which time the following results were obtained upon analysis:—

Bulb A.	0.001397 grm. iodine, trace of alkali.
" B.	0.001935 " "
" C.	0.002286 " "free alkali.
" D.	0.00254 " "

As far as it was possible to judge from the colouration of the pulp, all these bulbs had liberated their maximum quantity of iodine some days before analysis. It will be noticed that the total weight of iodine liberated is very small in the above instances, never exceeding 0.007 per cent of the total iodine present, or 1.120 per cent of the quantity the oxygen in the bulb was able to liberate.

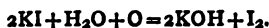
In an experiment made with potassium iodide which had been previously fused with charcoal, about 30 grms. of the salt were fused and dissolved in 100 c.c. of water. 40 c.c. of this solution was sealed in a bulb, and found after twenty-five days to be entirely free from iodine; 50 c.c. were sealed in another bulb with five sheets of paper reduced to pulp, and in this case after the same

* Read before the British Association (Section B), Ipswich Meeting, 1895.

exposure 0.001651 grm. of free iodine was found, the liquid being free from alkali.

If the air above the iodide solution in the tube is displaced by means of oxygen more iodine is liberated, and the maximum effect seems to be reached earlier; but I have not at present made sufficient experiments to trace any relation between the total quantity of oxygen present and the amount of iodide decomposed. Hydrogen, on the other hand, reduces the quantity of I_2 liberated, and if the oxygen is entirely removed from both the bulb and the solution I have no doubt that the iodide would remain perfectly undecomposed, although at present I have not succeeded in obtaining this theoretical result.

The equation for the reaction is most simply written:—



I hope to show presently that this does not completely represent the reaction, but, allowing that it gives the first stage of the decomposition, the reason for the very marked increase in the quantity of iodine liberated when cellulose is present becomes apparent, for the iodine set free by the above reaction should, and doubtless to a considerable extent does, re-combine with the potassium hydrates formed, producing a mixture of iodide and iodate. If, however, any substance is present which will combine with the alkali, removing it from the sphere of action, the oxidation is enabled to proceed without the subsequent combination of the liberated iodine. The absence of alkali in the solutions containing sufficient cellulose, and its presence when cellulose is either absent or present in small quantities, seems conclusive evidence that the increase in the amount of the iodide decomposed in presence of this substance is due to the removal of the alkali.

In order to obtain prints on paper by the decomposition of potassium iodide, I at first used a frame like that sold in toy-shops as a drawing-slate; more recently, however, I have used one exactly like the ordinary photographic printing-frames. The paper must not be too absorbent, and one with a smooth surface answers best; although I have been able to obtain fine proofs from ordinary negatives, the detail is too rough for these to be satisfactory, and consequently I have generally employed a negative made by cutting out a device in paper, fastening this to a sheet of glass, and varnishing. The best strength for the solution appears to be one containing about 1 part of the salt dissolved in 8 parts of water, a weaker solution requiring a much longer exposure, whilst if a stronger solution is used the ground of the resulting print is apt to become too dark. If a sheet of note-paper is moistened with the solution, and at once placed in the frame, it will, in about five minutes in diffused daylight, become printed in a light chocolate and pink colour, with the device cut out of the negative; if the exposure is prolonged the colour becomes much darker, and at the same time, owing to the spontaneous decomposition of the salt, the parts unexposed to the light become more or less deeply tinted; the exposed part is, however, always so much darker than the rest that the print stands out well. If the paper is allowed to dry in the dark after being saturated, it assumes a faint chocolate tint, and when placed in the frame and exposed for about four hours becomes printed in a dark chocolate, although it shows no signs of darkening for some time after a similar sheet of damp paper has become deeply marked. If a piece of paper, after being printed to a chocolate colour, is moistened with water, the colour of the print at once changes from chocolate to blue, and even if it is still damp when removed from the printing-frame the colour is never blue until water has been added to it. In order to arrive at some definite conclusion concerning the nature of the change occurring, I attempted, by means of a solution of iodine, to imitate the colour produced during exposure of the saturated paper to light; using at first a solution of iodine in an aqueous one of potassium iodide, I obtained, when it was poured over a sheet of writing-

paper, a stain which varied according to the concentration of the solution from blue to bluish-black; even when the solution was so dilute that in some lights it was difficult to see any mark, the stain upon the paper was always blue. I next used solutions of the element in benzene, carbon disulphide, chloroform, and alcohol: when these solutions were poured over paper, stains were produced which varied with the strength of solution from yellowish-brown to walnut. In other words, whilst the colour of the exposed paper was always tinged with pink in all attempts to imitate this, I obtained a blue colour if I used an aqueous, or a yellow colour if I used an anhydrous, solution of iodine.

I may here mention that all the note-paper I have examined contained starch, and that this solution only produces the well-known so-called iodide of starch in the presence of water; this latter fact may be shown by passing an anhydrous solution of iodide over paper coated with starch, when a brown stain is produced, which becomes blue, however, upon the addition to it of water. This explained the difference in the colour of the stains produced in the various solutions of iodine, but it did not help to indicate the action of light upon the potassium iodide; in fact, it made it rather more difficult, as it appeared to show that the colour of the prints was not due to the presence of free iodine; the only probable conclusion was, therefore, that the iodine combined at the moment of liberation with the still unaltered potassium salt, forming the tri-iodide or some similar compound. If this compound colours paper a pinkish chocolate, and is decomposed into its constituents by water, an explanation is at hand to account for the observed phenomena. To test whether this was the case, a little iodine was added to a solution of starch, and to the blue liquid thus obtained a concentrated solution of potassium iodide was added; the colour, however, remained unaltered, and after a large number of experiments I came to the conclusion that the amount of water necessary to bring the starch into solution was more than enough to decompose any higher iodide which might be found; the experiment was therefore varied by adding to a piece of solid starch which had been coloured pink by the addition of iodine in alcoholic solution a few drops of a saturated solution of potassium iodide; the colour of the starch deepened, but did not turn blue. I then took a piece of paper which was coloured blue by the presence of a small quantity of starch iodide, and added to it a very concentrated solution of potassium iodide; the blue colour changed to one approximating very closely indeed to that obtained by the action of light upon the iodised paper. This experiment seemed to justify the hypothesis that the colour of a piece of iodised paper after exposure is due to the presence of potassium tri-iodide or some similar compound.

In order to fix a print obtained upon the iodised paper, it is washed for a short time in running water; if the washing be too long continued, or if the paper be allowed to remain in a dish of water, the iodine dissolves and the proof is, of course, lost; lead acetate in very dilute solution is now poured over the paper, which is then again washed. If the print fixed in this manner is left it will begin at once to fade, and in a few days, or even hours, no trace of the design will be visible; if, however, a coat of size is put over it, and this followed by one of a hard varnish, the stability of the print is very much increased, and I have specimens which are more than three years old and are still distinct.

I have up to this point mentioned only the behaviour of potassium iodide when exposed to light, as the salt is the most easily obtained in a comparatively pure condition; it is the one with which I have chiefly worked. I have, however, made qualitative experiments upon the iodides of sodium, calcium, strontium, barium, zinc, cadmium, and iron.

Sodium iodide was bought as pure, and was probably no more impure than the ordinary potassium salt; it yielded a print of the same depth of colour as that ob-

tained from potassium iodide in considerably less time. As far, however, as could be judged from qualitative experiments, the maximum iodine was liberated about the same in each case.

Calcium, strontium, and barium iodides were obtained by adding the metallic carbonate to hydriodic acid which was free from iodine; the solutions, after filtering, were neutral and gave no colouration with starch.

Barium iodide gave a decided print in about ten minutes, and after an exposure of about two hours a strong print was obtained, which was, as in the case of the potassium salt, at first chocolate-coloured, turning blue on the addition of water.

Strontium iodide appears to be more sensitive to the action of light than the barium salt, a strongly-coloured proof being obtained after an exposure of about an hour.

Calcium iodide appears to be even more sensitive to the light than the strontium salt; in fact, the amount of iodine liberated seemed to vary roughly inversely as the atomic weight of the metal with which it is combined. I have experiments now in progress with a view to testing this.

Zinc iodide was obtained by placing 4 grms. of iodine in a flask together with metallic zinc and a little water. After standing in a warm place for a couple of days, the colour of the solution was discharged and when filtered and at once tested for iodine, it proved to be free from this element. The solution was made up to about 50 c.c., and paper was saturated with it as in the previous experiments. In all cases distinct proofs were obtained, but as the solution is exceedingly unstable, the unexposed portions were much discoloured, making the device more difficult to read.

Ferrous iodide was obtained in a similar manner to the zinc salt; iron-filings and iodine being warmed together, the filtered liquid was colourless, and gave no colouration with starch. It is, apparently, less sensitive to the action of light than the other soluble iodides, but I have obtained distinct prints when using it. The exposed parts are, of course, as in the case of the zinc salt, much discoloured owing to the spontaneous decomposition of the compound.

Cadmium iodide differs from all the other iodides I have examined, inasmuch as it gives a blue and not a pink print, it would thus appear that this element alone is unable to form a higher iodide.

THE RESPIRABILITY OF AIR IN WHICH A CANDLE-FLAME HAS BURNT UNTIL IT IS EXTINGUISHED.*

By FRANK CLOWES, D Sc.

At the last meeting of the British Association the author stated the composition of artificial mixtures of nitrogen and of carbon dioxide with air, which were just able to extinguish various flames. It was found that the flames of ordinary candles and lamps were extinguished by mixtures which contained on an average about 16.5 per cent of oxygen and 83.5 per cent of the extinctive gases. A flame of coal gas, however, required for its extinction a mixture still poorer in oxygen, and containing 11.3 per cent of oxygen and 88.7 per cent of the extinctive gases. These results have since been confirmed by a different method.

The method consisted in allowing the flames to burn in air inclosed over mercury until they were extinguished; the remaining extinctive atmosphere was then subjected to analysis, when its composition was found to be practically identical with that previously obtained from the artificial mixtures. An analysis of air expired from the lungs proved that it was also of the same composition as

that which extinguished the flame of an ordinary candle or lamp.

The average percentage composition of expired air and of air which extinguishes a candle-flame is as follows:—Oxygen, 15.9; nitrogen, 80.4; carbon dioxide, 3.7.

Now an atmosphere of this composition is undoubtedly respirable. Physiologists state that air may be breathed until its oxygen is reduced to 10 per cent. The maximum amount of carbon dioxide which may be present is open to question, but it is undoubtedly considerably higher than 3 per cent. Dr. Haldane maintains that the above atmosphere is not only respirable, but would be breathed by a healthy person without inconvenience of any kind; he further states that no permanent injury would result from breathing such an atmosphere for some time.

The conclusion to be drawn from these facts is, that an atmosphere must not be considered to be dangerous and irrespirable because the flame of an ordinary candle or oil-lamp is extinguished by it. The view is very generally advanced that a man must on no account venture into air which extinguishes the flame of a candle or of a bundle of shavings. It will be seen that this precaution may deter one from entering an atmosphere which is perfectly safe and respirable, and from doing duty of a humane or necessary character.

An atmosphere which extinguishes a coal-gas flame, however, appears to approach closely to the limit of respirability, as far as the proportion of oxygen which it contains is concerned. Hence the coal-gas flame appears to be a more trustworthy indicator of respirability than the flame of a candle or oil-lamp.

Undoubtedly the candle and lamp flames should be discarded as absolute tests of respirability of air.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

[THE complete works of the late J. S. Stas have recently been published at Brussels. They contain several memoirs on important points of chemistry and physics which are there published for the first time. Among these none equal in interest that entitled "*Recherches Chimiques et Etudes Spectroscopiques sur différents Corps Simples*." In the following pages we commence the translation of this memoir, and we propose to continue its publication from week to week till completed].

CHAPTER I.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF SODIUM, POTASSIUM, LITHIUM, CALCIUM, STRONTIUM, BARIUM, AND THALLIUM.

Introduction.

In undertaking these chemical works and spectroscopic studies, my object was to ascertain whether I could cause, by increasing the temperature or the intensity of the electric current, and contrary to what is generally admitted, a correlation among the characteristic bands of the luminous spectra of compounds of sodium, potassium, lithium, calcium, strontium, barium, and thallium, in such a state of purity as the improvements in the methods of chemical analysis permit me to actually obtain these bodies.

I was well aware that if my experiments failed, after having taken great pains and having devoted to this work an amount of time which I might perhaps have used more profitably, I should add nothing to the sum of our spectroscopic knowledge. Still, I should free science from an hypothesis which has led astray, and may again lead astray, many clever men; it seemed to me that this was just as much helping to advance *real* knowledge.

Chemical analysis is generally recognised as being

* Read before the British Association (Section B), Ipswich Meeting, 1895.

unable to detect the presence of sodium, still less to find the percentage of this metal, when it exists in a very small proportion in a given compound.

Since the memorable works of Messrs. Bunsen and Kirchhoff on spectrum analysis, chemists have almost invariably used this method of detecting the presence of sodium.

Whilst applying their method to the examination of soluble compounds obtained by the method of fractional crystallisations, the illustrious authors have found that, by this process, one can never entirely separate the sodium from the body with which it is mixed; one must employ simultaneously a chemical reaction by which one can obtain an absolute separation. M. Bunsen and then M. Diehl were the first to practise this method, the latter on the advice of his illustrious master.

The occurrence of the sodium line in the spectrum of nearly all compounds led Mr. Lockyer to believe that this metal is evolved by the dissociation of the elements of the bodies on which one is working. This hypothesis, if it were verified, would necessitate the overthrow of all the fundamental notions of the physico-chemical sciences.

However improbable it has appeared, as regards the majority of chemists who have done accurate work, the name of Mr. Lockyer, and the brilliant services which he has rendered to science by his spectroscopic researches, have induced me to submit his hypothesis to a critical examination, about which he has done me the honour of writing to me (1878).

The work that I have undertaken with potassium has also had as an object the solving by its means the problem of ascertaining if it is really possible to procure a chloride of potassium which does not give, under any circumstances, any indication of the presence of sodium, and of obtaining this compound in such a state of purity, that the result arrived at in determining its atomic weight in regard to that of silver would leave no doubt in anybody's mind.

My investigations have included the compounds of potassium, sodium, thallium, lithium, calcium, strontium, and barium.

I have borne in mind the fact that the results depend as much on the medium in which the metallic compounds are enclosed, as on their accidental impurities.

This medium being, for example, air, I have found or I have not found sodium, according as the air gives or does not give indications of the presence of this metal. This fact has led me to examine the air by means of the spectroscope.

Respecting the Characteristics Impressed by the Surrounding Air on Hydrogen Flames, Illuminating Gas, Hydrogen Blowpipe Flame, Oxy-hydrogen Blowpipe Flame, Oxy-carbo-hydrogen Blowpipe Flame, and Ordinary Flame, and on the Electric Discharge and Electric Arc.

I must commence my statement with the observations which I have made on air.

What I am about to say relates exclusively to the air of Brussels, to that in the "Musée de l'Industrie," where I have worked, and in my own laboratory. Amongst the observations which I have to mention are many familiar to chemists engaged in spectrum analysis; but I must recapitulate them in order to make my statement as complete as possible.

The room in the Musée de l'Industrie in which I have carried on my spectroscopic researches measures about 1143 cubic metres. It can be made into a dark room, as I have had occasion to do daily during my researches.

During the time occupied by my work the room was placed entirely at my disposal.

When the external air is quiescent, and has been for several days saturated with moisture, a state of things which occurs in Brussels from the end of October to the middle of December, and the room, previously washed out with a copious supply of water, and properly ventilated

from the external saturated atmosphere, has been kept closed for twelve or eighteen hours, a time necessary for the deposition of particles of dust, mineral matters, &c., the jet of gas, mingled with a suitable supply of air, issuing from a well made Bunsen burner, terminated by a pipe of platinum, silver, or gold, free from sodium, or even a pipe of brass, well cleansed inside and out, burns with a flame of pure rich blue, in which it is impossible to detect the presence of sodium by any spectroscope. Let one then make a prismatic analysis of the top, middle, and base of the luminous cone, the diameter of which varies from 1 to 1½ c.m. and the height from 10 to 25 c.m.

If one introduces, by means of a loop of fine platinum wire, into the middle of the height of the flame, some dilute hydrochloric acid or some pure chloride of ammonium, the colour of the upper half changes immediately; it turns green, and the intensity of the colour varies in proportion to the quantity of hydrochloric acid or chloride of ammonium introduced. In the flame thus rendered visible, it is impossible to recognise by prismatic analysis the slightest trace of the spectrum of sodium, or of a partially burnt hydrocarbon.

Having substituted for the Bunsen burner a blowpipe of platinum or silver, previously cleansed from all sodium particles, and for the illuminating gas properly purified hydrogen, one notices that this gas burns in pure air with a flame so colourless, and with such a faint luminosity, that in the dark the eye can scarcely perceive it. One cannot discern in any part of this flame the slightest indication of the sodium "D" line, or of a continuous spectrum.

The introduction of hydrochloric acid or of pure ammonia into hydrogen burning in pure air, gives directly to its colourless flame a tint of a livid greenish yellow, similar to that seen when burning hydrogen in chlorine. The prismatic analysis of this flame does not enable one to detect the presence of the sodium line or of a continuous spectrum.

In the blowpipe, with a pipe of pure platinum, cleansed inside and out from sodium particles, fed with a mixture in proper proportions of illuminating gas, or of hydrogen and air, or of pure hydrogen and oxygen, spectroscopic observation demonstrates in all cases the complete absence of the sodium "D" line, whatever may be the part of the flame examined. After the introduction of hydrochloric acid, which greatly alters the colour of these flames, one can find no trace of the sodium line.

To complete these proofs, I must add that, in the darkened room, with pure air, spectrum analysis does not enable one to detect the appearance of any spectrum, not even a glimmer from the upper two-thirds of a flame from a well made Bunsen burner,* terminated by a platinum tube, or from a flame of from 10 to 25 c.m. length issuing from a platinum blowpipe supplied with air or with pure oxygen.

The spectrum only appears from this part of the flame or blowpipe flame when one puts there a solid non-volatile body, and in this case the spectrum produced is continuous, as we know.

As regards the blowpipe flame which results from the combustion of an excess of pure hydrogen in equally pure oxygen issuing under pressure from a platinum burner, frequent observations permit me to state that, in the portions of this flame where the temperature is not high

* When the burner is faultily made, as is often the case, the flame, instead of consisting of a single cone surrounded by a barely visible but very hot envelope, resolves itself into two cones, extending from the base almost to the apex; an internal cone, slightly luminous and purple, surmounted by a second cone of pure blue in pure air, surrounded again by a barely visible envelope where the combustion of carbon takes place. In the flame from this badly-made burner, the second cone agrees with the conditions mentioned above; that is, in the absence of any spectrum, although the inside cone gives to spectrum analysis the partial spectrum of burning hydrocarbons, to which I shall return later on. *Whichever was the burner used, I have always placed in the barely visible external envelope of the flame the body which I wished to put in it for the purpose of making a spectrum analysis.*

enough to bring the platinum well up to melting-point, spectrum analysis does *not* enable me to see a spectrum. The place of the spectrum is occupied entirely by a dark band, even when the width of the slit in the collimator of the spectrocope exceeds the limit necessary for distinct vision of the dark lines in the solar spectrum. As soon as the temperature of the flame reaches the fusing-point of platinum, the hydrogen becomes incandescent; its colour becomes a pale or sky blue. Spectrum analysis then shows the appearance of a continuous spectrum, yet without the formation of bands or lines. It resembles that from the upper third of a blowpipe flame in which the hydrogen has not reached the point of incandescence. As a matter of fact, the flame which issues from an oxy-hydrogen burner under more or less pressure, is composed of two cones superposed, as in the case of a badly made Bunsen burner, of a lower internal cone coloured light blue in pure air, merging into the upper colourless cone, when it consists of the oxyhydrogen flame fed with an excess of hydrogen and oxygen.

Spectrum analysis of this lower internal cone gives a continuous spectrum, destitute of bands or lines, and whose brightness increases continuously from the point up to the part where the temperature is at a maximum and in a condition to keep iridium and rhodium fused. I shall return later on to the subject.

On substituting for the hydrogen some illuminating gas or a very volatile hydrocarbon,—for instance, petroleum naphtha or similar body in the state of vapour, issuing from a platinum burner,—one notices analogous facts as regards the lower cone, which is always coloured blue. The spectrum analysis of this cone allows one to see a continuous spectrum crossed with bands and lines of exceeding brilliance. The bands and lines are numerous. Towards the portion of the lower cone, where the light of the spectrum is most dazzling, the temperature is so high that rhodium and iridium can be kept fused. I shall return to this spectrum later on.

To resume—If one makes a prismatic analysis of that part of the blowpipe flame of hydrogen and air, of oxyhydrogen, or of oxyhydrocarbon, in which platinum begins to melt or in which it is quite melted, or in which iridium can be kept in a state of fusion, whether there be either no spectrum or one of great brilliance; in any case the spectrum analysis does not enable one to detect the presence of the sodium D line, when the air in which the experiment takes place is pure, or at least has a given relative degree of purity; when the elements used to produce the flame are pure; and, lastly, when the apparatus itself yields no trace of sodium.

I shall certainly not surprise those who have done any spectrum analysis when I say that I have met with the greatest difficulties in verifying, under the conditions given, the facts written above, simple as they seem.

(To be continued).

REPORT OF COMMITTEE ON ATOMIC WEIGHTS, PUBLISHED DURING 1894.*

By F. W. CLARKE.

(Concluded from p. 167).

THALLIUM.

Two determinations of atomic weight were made by Wells and Penfield to ascertain the constancy of the element as such (*Am. Journ. Sci.*, 3, xlvii, 466). The nitrate was fractionally crystallised until about 1-20th remained in the mother-liquor, while another twentieth had been subjected to repeated re-crystallisation. Both fractions were converted into thallium chloride, which was dried at 100°, and in both the chlorine was estimated

by weighing as silver chloride on a Gooch filter. The results were as follows:—

	TlCl.	AgCl.	At. wt. Tl.
Crystals	3.9146	2.3393	204.47
Mother-liquor ..	3.3415	1.9968	204.47

Calculated with Ag=107.92 and Cl=35.45.

In the report for 1893 Lepierre's work on thallium was given, and the last value cited was Tl=203.00, varying widely from the rest of the series and affecting the mean. The mean stated by Lepierre was 203.62, and as found by me was 203.57. Lepierre (*Bull. Soc. Chim.*, 3, xi., 423) now calls attention to the fact that his value 203.00 was a misprint for 203.60, and that his mean was therefore correctly given. He also gives additional details relative to his work.

BISMUTH.

The long-standing controversy between Schneider and Classen over the atomic weight of bismuth has led to a new set of determinations on the part of Schneider (*Journ. Prakt. Chem.*, 2, l., 461). The old method was still used; namely, of converting the metal into the trioxide by means of nitric acid and subsequent ignition of the nitrate; but the metal itself was carefully purified. Results as follows:—

Wt. Bi.	Wt. Bi ₂ O ₃ .	P.c. Bi in Bi ₂ O ₃ .
5.0092	5.5868	89.661
3.6779	4.1016	89.648
7.2493	8.0854	89.659
9.2470	10.3142	89.662
6.0945	6.7979	89.653
12.1588	13.5610	89.660

Mean .. 89.657

If O=16, Bi ranges from 207.94 to 208.15, or in mean 208.05, confirming the earlier determinations.

TIN.

Incidentally to his paper on the white tin sulphide Schmidt gives one determination of the atomic weight of the metal (*Ber. d. Chem. Ges.*, xxvii., 2743).

0.5243 grm. Sn gave 0.6659 SnO₂. Hence Sn=118.48.

ANOMALOUS NITROGEN.

An important discovery has been made by Lord Rayleigh, who finds that nitrogen obtained by purely chemical methods is perceptibly lighter than that from atmospheric air (*CHEM. NEWS*, lxi., 231, May 18, 1894). Equal volumes of the gas, variously prepared, weighed as follows:—

By passing NO over hot iron	2.30008
" N ₂ O	2.29904
" AmNO ₂	2.29869

For nitrogen from air he found:—

From air passed over hot iron	2.31003
" " through moist FeO ₂ H ₂	2.31020
" " over hot copper	2.31026

Investigating the cause of this anomaly, with the co-operation of Ramsay, Rayleigh came to the astonishing results communicated a few months later to the British Association. It was found, in short, that atmospheric air contains a gas heavier than nitrogen, and hitherto unknown. Its density, in a sample as pure as could be obtained, was 19.09, and it was characterised by extraordinary inertness. Whether it is a new element, or allotropic nitrogen, N₃, remains to be determined. The work is cited here because it shows that the density of nitrogen as hitherto determined can give no trustworthy value for the atomic weight of the element.

MISCELLANEOUS NOTES.

Some data bearing upon the atomic weight of tellurium are given by Gooch and Howland (*Am. J. Sci.* [3],

* From the *Journal of the American Chemical Society*, vol. xvii., No. 5. Read at the Boston Meeting, Dec. 28, 1894.

xlviii., 375). As the homogeneity of tellurium is still uncertain, I omit their details.

Wanklyn's attempt to show that the atomic weight of carbon is not 12, but 6, was noted last year. He has since published more on the subject in a paper on Russian Kerosene (*Phil. Mag.*, [5], xxxvii., 495), and the matter was also discussed at the Oxford meeting of the British Association (*CHEM. NEWS*, lxx., 87, Aug. 24, 1894).

In a communication upon the Stasian determinations (*Compt. Rend.*, cxviii., 528), Hinrichs discusses the availability of silver as a secondary standard in the scale of atomic weights. He makes silver, chlorine, bromine, iodine, and sulphur all Proutian in value. Hinrichs also has published his views upon atomic weights *in extenso* in book form ("The True Atomic Weight of the Chemical Elements, and the Unity of Matter," by Gustavus Detlef Hinrichs, St. Louis, 1894).

In conclusion I submit a table of atomic weights revised to January 1, 1894. O=16 is still retained as the base of the system; but I hope that in another year it will be practicable to return to H=1.

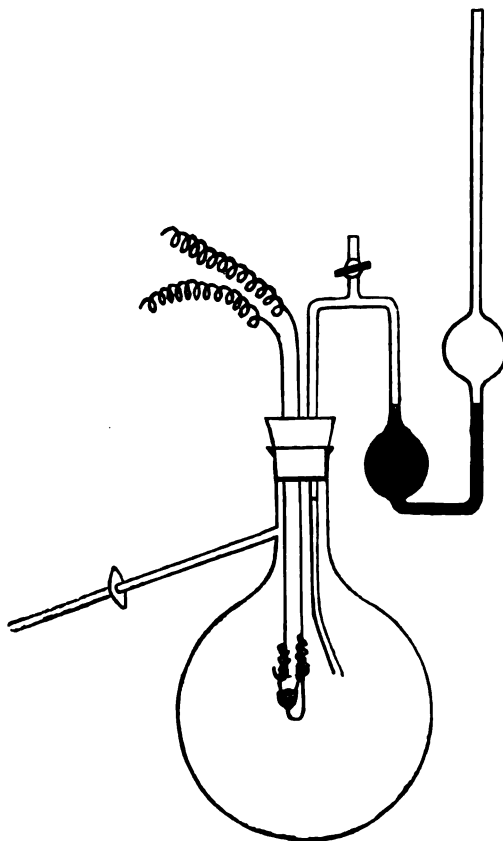
Name.	Atomic weight.
Aluminium	27'
Antimony	120'
Arsenic	75'
Barium	137'43
Bismuth	208'
Boron	11'
Bromine	79'95
Cadmium	112'
Cæsium	132'9
Calcium	40'
Carbon	12'
Cerium	140'2
Chlorine	35'45
Chromium	52'1
Cobalt	59'5
Columbium	94'
Copper	63'6
Erbium	166'3
Fluorine	19'
Gadolinium	156'1
Gallium	69'
Germanium	72'3
Glucinum	9'
Gold	197'3
Hydrogen	1'008
Indium	113'7
Iodine	126'85
Iridium	193'1
Iron	56'
Lanthanum	138'2
Lead	206'95
Lithium	7'02
Magnesium	24'3
Manganese	55'
Mercury	200'
Molybdenum	96'
Neodymium	140'5
Nickel	58'7
Nitrogen	14'03
Osmium	190'8
Oxygen	16'
Palladium	106'5
Phosphorus	31'
Platinum	195'
Potassium	39'11
Praseodymium	143'5
Rhodium	103'
Rubidium	85'5
Ruthenium	101'6
Samarium	150'
Scandium	44'
Selenium	79'
Silicon	28'4

Name.	Atomic weight.
Silver	107'92
Sodium	23'05
Strontium	87'66
Sulphur	32'06
Tantalum	182'6
Tellurium	125'
Terbium	160'
Thallium	204'18
Thorium	232'6
Thulium	170'7
Tin	119'
Titanium	48'
Tungsten	184'9
Uranium	239'6
Vanadium	51'4
Ytterbium	173'
Yttrium	89'1
Zinc	65'3
Zirconium	90'6

LECTURE APPARATUS.

By Dr. W. R. HODGKINSON, F.R.S.E.

In the *Annalen der Chemie* (vol. cclxxiv., p. 3) Volhard describes an apparatus for certain lecture purposes. I have had an apparatus of very similar form and for the same purposes in use in my lectures at the Royal Military Academy for the past eight years or more.



One or two additions or improvements were added some time ago by my assistant, Mr. J. Young, A.R.C.S.

The substance to be burnt can be fired by the electric wires; the particular form of gauge obviates any danger of gases escaping owing to excessive expansion at the moment of burning. It is, as will be seen, only a large distilling flask with a stopcock sealed on the tube. Oxygen may be driven in and through by means of the two taps, after the substance has been put in the cup. This is an advantage generally.

As a rule the rubber stopper is wired down and mercury used in the gauge.

The apparatus can be used in a rough quantitative way.

Royal Military College, Woolwich.

ON THE CONSTITUENTS OF THE GAS IN CLEVEITE.

By C. RUNGE and F. PASCHEN.

We have investigated the spectrum of the gas discovered in the mineral cleveite by Ramsay, and have found it to be most regular. It consists of six series of lines, the intensity of the lines in each series decreasing with decreasing wave-lengths. Similar series of lines have been observed in many spectra. The first series was discovered by Dr. Huggins in the ultra-violet spectra of a number of stars. It proved to belong to hydrogen, and to be the continuation of the four strong hydrogen lines in the visible part of the spectrum. Johnstone Stoney had already shown that three of the wave-lengths of the visible hydrogen lines were most accurately proportional to the values $9/5$, $4/3$, $9/8$, when Balmer discovered that these values were given by the formula—

$$\frac{m^2}{m^2 - 4}$$

for $m = 3, 4, 6$, and that the other wave-lengths of the series were proportional to the values obtained by substituting for m the other entire numbers greater than three. The series has now been followed from $m=3$ to $m=20$, the lines growing weaker and weaker to the more refrangible side, and approaching each other closer and closer. The formula shows that they approach a definite limit for large values of m . This is seen more clearly when we consider wave-numbers instead of wave-lengths, which according to the formula would be proportional to—

$$1 - \frac{4}{m^2}$$

Many series of lines similar to the hydrogen series were discovered by Liveing and Dewar. They have called them harmonic series, and have compared them to the series of over-tones of a vibrating body. They have been further studied by Rydberg and by Kayser and Range. We cannot here enter into any detailed account. We only want to explain so much as to make the conclusions understood which we have drawn from the spectrum of the gas in cleveite. The wave-lengths λ of the lines belonging to the same series are always approximately connected by a formula somewhat similar to Balmer's—

$$1/\lambda = A - B/m^2 - C/m^4.$$

A determines the end of the series towards which the lines approach for high values of m , but does not influence the difference of wave-numbers of any two lines. B has nearly the same value for all the series observed, and C may be said to determine the spread of the series, corresponding intervals between the wave-numbers being larger for larger values of C . As B is approximately known, two wave-lengths of a series suffice to determine the constants A and C , and thus to calculate approximately the wave-lengths of the other lines. It was by this means that we succeeded in disentangling the spectrum of the gas in cleveite, and showing its regularity.

In the spectrum of many elements two series have been observed for which A has the same value, so that they both approach to the same limit. In all these cases the series for which C has the smaller value, that is to say which has the smaller spread, is the stronger of the two. In the spectrum of the gas in cleveite we have two instances of the same occurrence. One of the two pairs of series, the one to which the strong yellow double line belongs, consists throughout of double lines whose wave-numbers seem to have the same difference, while the lines of the other pair of series appear to be all single. Lithium is an instance of a pair of series of single lines approaching to the same limit. But there are also many instances of two series of double lines of equal difference of wave-numbers ending at the same place as sodium, potassium, aluminium, &c. There are also cases where the members of each series consist of triplets of the same difference of wave-numbers as in the spectrum of magnesium, calcium, strontium, zinc, cadmium, mercury. But there is no instance of an element whose spectrum contains two pairs of series ending at the same place. This suggested to us the idea that the two pairs of series belonged to different elements. One of the two pairs being by far the stronger, we assume that the stronger one of the two remaining series belongs to the same element as the stronger pair. We thus get two spectra consisting of three series each, two series ending at the same place, and the third leaping over the first two in large bounds and ending in the more refrangible part of the spectrum. This third series we suppose to be analogous to the so-called principal series in the spectra of the alkalis, which show the same features. It is not impossible, one may even say not unlikely, that there are principal series in the spectra of the other elements. But so far they have not been shown to exist.

Each of our two spectra now shows a close analogy to the spectra of the alkalis.

We therefore believe the gas in cleveite to consist of two, and not more than two, constituents. We propose to call only one of the constituents helium, the one to which the bright yellow double line belongs, whose spectrum altogether is the stronger one, while the other constituent ought to receive a new name.

We have confirmed this rather hypothetical conclusion by the following experiment:—The connection leading from our supply of cleveite gas to the vacuum tube contained a side branch parting from it and joining it again. There were stopcocks on either side of the side branch, and a third one in the side branch. In the main tube between the ends of the side branch a plug of asbestos was tightly inserted. To prepare the vacuum tube only the tap leading to the supply was closed, the whole space up to this tap being carefully evacuated. Now the side branch was closed, and the tap leading to the supply was opened. Then we observed that the light of the electric discharge in the vacuum tube was at first greenish, and after a while grew yellow. By cutting off the current of gas after a sufficiently short time, we succeeded in making a vacuum tube which remained greenish. On examining it in a small spectroscopic with which we could overlook the whole spectrum, we found that the intensities of the lines had changed. The yellow line was scarcely as bright as the green line 5016, and the red line 7065 had apparently decreased relatively to 7282 and 6678, although it was still stronger than 7282. The two lines that had decreased in intensity belong to the second set of series, while the others are members of the first set. The other visual lines of the second set could not very well be examined, because they are more in the violet part.

This observation confirms our spectroscopic result. The gas in cleveite may be taken to be a mixture of two gases of different density, of which the lighter one is more rapidly transmitted through the plug of asbestos. There is, however, the objection to be raised, that in the green tube the pressure is less, and that the difference of inten-

sities is due to the pressure being different. This must be further inquired into.

We were not satisfied with the visual observation of the change of intensities in our green tube, but thought it desirable to test the conclusion by the bolometric measurement of the two lines that we have discovered in the ultra-red part of the spectrum. If we were right, the ultra-red line of smaller wave-length, which belongs to the second set of series, ought to have decreased in intensity relatively to the other ultra-red line. This we found to be so indeed. In the yellow tubes the intensity of the smaller wave-length was to that of the other on an average as 3 to 1, while in the green tubes it was as 1·8 to 1. This confirmation we consider the more valuable as it does not depend on any estimation which may be biased by the personal opinion of the observer, but is based on an objective numerical determination.

Another confirmation may be gathered from the spectrum of the sun's limb and that of several stars. Let us confine our attention to the six strongest lines in the visible part of the spectrum:—

7066, 6678, 5876, 5016, 4922, 4472.

The first, third, and sixth belong to the second set of series; the second, fourth, and fifth to the first set. These six lines have all been observed in the spectrum of the sun's limb, as Norman Lockyer and Deslandres have pointed out. Now, according to their appearance in the spectrum of the sun's limb, they may be classed in two groups, one group being always present, the other group being sometimes present. C. A. Young long ago called attention to the difference in the frequency of appearance of the chromospheric lines. He has given them frequency numbers, roughly estimating the percentage of frequency with which the lines were seen during the six weeks of observation at Sherman in the summer of 1872. According to Young, 7066, 5876, 4472 have the frequency number 100, while 6678, 5016, 4922 have the numbers 25, 30, 30, showing that one of the two constituents was always present, while the other was only seen about once in every four cases.

The lines of both constituents have been observed in the spectra of a considerable number of stars, β , δ , ϵ , ζ , γ Orionis, α Virginis, β Persei, β Tauri, η Ursæ majoris, β Lyrae. In the spectrum of β Lyrae thirteen lines have been identified with certainty. But the most interesting case in point is the spectrum of Nova Aurigæ, that wonderful star whose sudden appearance was announced to astronomers in 1892 by an anonymous post-card. In the spectrum of Nova Aurigæ the two lines 5016 and 4922 were very strong, while 4472 was weak, and 5876 has only been seen by Dr. Huggins, we believe only on one occasion, and appears to have been very weak. Now 5016 and 4922 belong to the lighter constituent, and are together with 6678 the strongest lines in the visible part of the spectrum; while 5876 and 4472 are the strongest lines of the other constituent in the visible part of the spectrum. In Nova Aurigæ, therefore, the lighter constituent gave a much brighter spectrum than helium proper. But there may here be raised an objection, which indeed we do not know how to refute. Why has the line 6678 not been observed? It is a pity that the red part of the spectrum cannot be more easily photographed. Nova Aurigæ has now become very weak, and besides the spectrum is quite altered, so that we shall never know whether the red line 6678 was really absent or has only escaped notice.

From the fact that the second set of series is on the whole situated more to the refrangible part of the spectrum, one may, independently of the diffusion experiment, conclude that the element corresponding to the second set is the heavier of the two. In the spectra of chemically related elements like Li, Na, K, Rb, Cs, or Mg, Ca, Sr, or Zn, Cd, Hg, the series shift to the less refrangible side with increasing atomic weight. But it appears that in the spectra of elements following each

other in the order of their atomic weights in a row of the periodic system like—

Na, Mg, Al;
K, Ca;
Cu, Zn;
Rb, Sr;
Ag, Cd, In;

the series shift the opposite way, so that the spectrum of the element of greater atomic weight is as a whole situated further to the more refrangible side. Now in our case the density of the gas has been determined by Langlet (published by Clève) and by Ramsay to be about double the density of hydrogen. Assuming the atomic weights of the two constituents to be between that of lithium and that of hydrogen, they would both belong to the same row of the periodic system, and therefore the more refrangible set of series would correspond to the greater atomic weight.

For convenience of reference all the observed lines are given in the following table, the wave-lengths being abridged to tenth-metres.

Lighter Constituent.

Principal series.	First subordinate series.	Second subordinate series.
20400	6678	7282
5016	4922	5048
3965	4388	4438
3614	4144	4169
3448	4009	4024
3355	3927	3936
3297	3872	3878
3258	3834	3838
3231	3806	3808
3213	3785	

Heavier Constituent (Helium proper).

	Double lines.	Double lines.
11220	5876	7066
3889	4472	4713
3188	4026	4121
2945	3820	3868
2829	3705	3733
2764	3634	3652
2723	3587	3599
2696	3555	3563
2677	3531	3537
	3513	3517
	3499	3503
	3488	3491
	3479	3482
	3472	
	3466	
	3461	

—Nature, September 26, 1895.

ON THE VAPOUR-TENSIONS OF MIXTURES OF VOLATILE LIQUIDS.*

By C. E. LINEBARGER.

(Continued from p. 170).

Calculation of Results.

In the calculations it is assumed that the laws of perfect or ideal gases may be applied to the mixtures of vapours; that is, the laws of Boyle, Gay-Lussac, and Dalton. Where not too much vapour is present in the gaseous mixture the legitimacy of this assumption is unquestionable; and even though this condition be not fulfilled, the

* Abridged from the *Journal of the American Chemical Society* vol. xvii., No. 8, August, 1895.

TABLE I.—Vapour-tensions of Pure Liquids.

Name of liquid.	Temperature.	Loss in grms.	Volume of loss in c.c.	Volume of air in c.c.	Internal pressure in m.m. Hg.	Barometer in m.m. Hg.	Tension of vapour in m.m. Hg.	Tension according to other observers.
Benzene	34°8'	1·3805	443·	1876	5	760	145·4	147·2 (Y)
Monochlorobenzene	34°8'	0·2291	5·1	1883	10	757	20·3	20·0 (Y)
Monobrombenzene	34°8'	0·1289	2·0	1888	10	757	8·0	8·0 (Y)
Toluene	34°8'	0·2451	67·6	1014	11	754	46·8	
"	34°8'	0·4672	128·9	1949	11	754	46·7	
Metaxylene (not especially purified) ..	34°8'	0·1080	25·8	1201	17	757	4·17	
"	34°8'	0·1085	25·9	1201	17	758	4·18	
Nitrobenzene	34°8'	0·0090	1·85	1210	23	757	1·16	
"	34°8'	0·0088	1·83	1207	21	757	1·15	
Carbon tetrachloride	34°8'	3·3803	5·55	1913	20	758	169·4	172·6 (R)
"	27°8'	2·4031	3·96	1908	18	756	130·0	130·8 (R)
Chloroform	35°0'	3·0320	64·48	1033	25	755	290·1	301·1 (R)
Ethyl iodide	34°8'	4·2091	683·	1913	20	756	199·0	206·0 (R)
"	27°8'	2·9760	483·	1918	22	756	152·2	154·7 (R)
Carbon bisulphide	20°0'	2·4541	777·4	1206	21	756	296·4	298·1 (R)
Methyl formate.. .. .	20°0'	5·1000	195·8	1196	16	756	469·4	
Acetic acid.. .. .	35°0'	0·2900	70·0	1960	20	760	26·3	26·5 (R&Y)

NOTE.—(Y) = Young, *Chem. Soc.*, lv., 486, 1889; (R) = Regnault, *Mémoires de l'Académie*, xxvii., 239, 1862; (R & Y) = Ramsay and Young, *Chem. Soc.*, xlix., 790, 1886.

approximation to accuracy may be sufficient (see "Comparison of the Vapour-tensions," &c.).

Calculation of Volume of Air passed through a Mixture.—In order to force the air in the measuring vessel through the liquid in the absorption-vessel, it is necessary that it be brought under a pressure equal to that of the atmosphere plus that required to vertically displace the liquid contained in the bulbs, the latter pressure varying with the density and amount of the mixture. The volume of the air under atmospheric pressure may be obtained then as follows:—

Let P represent the pressure of the atmosphere. Let P' represent the pressure which forces the air through the liquid. Let V' represent the volume of air under the pressure P+P'. Let V represent the volume of air under the pressure P.

According to Boyle's law, and inasmuch as the temperature remains constant,—

$$V = \frac{(P + P') V'}{P}$$

Calculation of Composition of Mixture of Liquid Vaporised.—As this calculation is simply one of quantitative analysis, it is not necessary to treat of its details.

Calculation of Partial Volumes of Mixtures of Vapours.—Let m represent the quantity of one component in the gaseous mixture. Let M represent its molecular mass. Let 22·32 represent the volume in litres of a grm.-molecule of hydrogen at the temperature 0° and under the pressure 760 m.m. Let α represent the coefficient of expansion. Let v_1 represent the volume of vapour at the temperature of the determination, t , and under the atmospheric pressure, p . We then have—

$$v_1 = 22\cdot32 \frac{m}{M} \times \frac{760 (1 + \alpha t)}{p}$$

Calculations of Partial Pressures of Components of Vapour Mixture.—Let v_1 represent partial volume of one component. Let v_2 represent partial volume of the other. Let v represent partial volume of air. Let p_1 represent partial pressure of one component. Let p_2 represent partial pressure of the other. Let p represent the atmospheric pressure.

In accordance with Dalton's law,—

$$p_1 = p \frac{v_1}{(v + v_1 + v_2)}$$

and—

$$p_2 = p \frac{v_2}{(v + v_1 + v_2)}$$

Comparison of the Vapour-tensions obtained by the Method herein Described and those obtained by other Methods.

Probably the best way to judge of the accuracy of the results obtained in the determination of the vapour-tensions of liquids according to the method described in this paper is to compare them with the results obtained by other investigators working by other methods. Also a criterion of accuracy is to be found in the more or less close concordance of duplicate experiments. In Table I. are given the necessary data of my experiments together with the results obtained by others. It was in some cases necessary to interpolate the results of others inasmuch as my results referred to a limited number of temperatures; the interpolations were made on a large scale, so as to avoid any slight inaccuracy. The original papers of Young and Regnault I am now unable to consult, and have to take their data as given in Landolt and Börnstein's "Physikalische - Chemische Tabellen" or other reproductions.

An inspection of the table shows a most excellent correspondence between my determinations of vapour-tensions and those of others, when the liquid is but slightly volatile, as in the case of the halogen substitution-products of benzene. But when, at the temperature taken for a determination, the elastic force of the vapour exceeds 100 m.m. of mercury, the correspondence becomes less close; and it is at once seen from the data that the greater the volatility of a liquid, the greater the discrepancy. Let us take carbon tetrachloride and ethyl iodide for examples, since determinations of their vapour-tensions were carried out at two different temperatures. For carbon tetrachloride the difference between Regnault's results and mine is $3\frac{1}{2}$ m.m. of mercury at 34°8' and $\frac{1}{2}$ m.m. of mercury at 27°8'; for ethyl iodide, the difference at 34°8' is $7\frac{1}{2}$ m.m. of mercury, and at 27°8' $1\frac{1}{2}$ m.m. of mercury. Other examples point to the same result.

The cause of this want of concordance between my results and those made by other methods has been hinted at in a discussion of the errors to which this method is subject. The assumption, made in the calculations, that the vaporous mixture may be treated as a mixture of ideal gases, cannot be maintained when the volume of the vaporised liquid forms more than a small fraction of the total volume of the gaseous mixture that leaves the absorption vessel. The vapour of ethyl iodide that was carried off by the air, occupied more than a fourth of the total volume, and the other volatile liquids also occupied relatively large volumes; the volumes of the vapours of the less volatile liquids, however, were but a small part of the volume of the air passed through the liquid. And,

as has been shown, the less volatile liquids give results perfectly concordant with those obtained by others. Duplicate determinations of the vapour-tensions of some of the liquids, as toluene, nitrobenzene, &c., give almost identical results.

It would not be difficult to apply a correction taking into account the greater volatility of some of the liquids. This I have not, as yet, done, as in certain details I wish to alter the apparatus so as to obtain even more accurate results; thus the use of mercury as the liquid for expelling the air from the measuring vessel would render the system of drying-tubes unnecessary; also, ground-glass joints are undoubtedly preferable to rubber connections. Although it is my intention to study and modify the apparatus further, I do not want to seem to "reserve" this subject of investigation; on the contrary, I would be most glad to see the apparatus tried and tested by others.

Although the results obtained by the employment of this method do not have, in the case of the more volatile liquids, the same degree of accuracy attainable by other methods, still they are suited to the requirements of an investigation of the vapour-tensions of mixtures of liquids, since both liquids, if their vapour-tensions be not too different, are affected alike by any weaknesses in the method, and the phenomenon observed permits of the drawing of theoretic conclusions. Yet I have been careful in the discussion of results to limit myself as much as possible to such as were of the same accuracy as results obtained by others; thus, my method can be counted upon to give results accurate to less than 1 m.m. of mercury when the vapour-tension does not exceed 100 m.m. of mercury, and to less than 2 m.m. of mercury when the vapour-tension is less than 150 m.m. of mercury; as can at once be seen by a comparison of the data due to Young (*loc. cit.*) and Regnault (*loc. cit.*) in the greater number of cases a closer correspondence than to within 2 m.m. cannot be found. However, the conclusions which I draw from my experiments would still hold if the error in the determination were several times greater than that admitted above, inasmuch as it affects each liquid in the same way, so that, while it may affect the absolute accuracy, its relative effect is but slight.

(To be continued).

NOTICES OF BOOKS.

Analytical Chemistry. By N. MENSCHUTKIN, Professor in the University of St. Petersburg. Translated from the Third German Edition, under supervision of the Author, by JAMES LOCKE. London and New York: Macmillan and Co. 1895. 8vo., pp. 512.

In noticing this work we must distinguish between the matter and the language. The author's instructions will be pronounced excellent by all competent chemists who may give them the necessary examination. We do not indeed, see that the author proposes any novel reaction or brings forward any new general method. But he lays due weight on the acquisition of the habit of *chemical thought*, which he justly pronounces the most important object of practical work. Mere mechanical study he appraises at a very low value, considering that it cannot in a single instance teach how to make a correct analysis, to say nothing about developing the faculty of chemical thought. He condemns the practice of allowing the student to enter upon analysis before he has been prepared by a thorough training in general chemistry. He insists that the necessary knowledge should be estimated not by the number of single and isolated facts with which he is familiar, but by the clearness with which he understands fundamental chemical phenomena and theories,—points not always duly appreciated by the routine examiner.

The work consists of two main parts, a qualitative and

a quantitative. The author holds that the student should in the outset devote himself to the former branch alone.

In a supplement to the section on qualitative analysis the author explains the use of the blowpipe,—which he remarks has almost completely disappeared from the laboratory with the introduction of the Bunsen gas-burner, though for the prospector and the traveller it retains all its former value,—of Bunsen's flame-reactions, which are here very fully expounded, and of spectrum analysis, which receives here an attention unusual in analytical manuals.

Prof. Menschutkin describes the spectroscopy of Bunsen and Kirchhoff (not Kirschhoff!), the reversal of the spectrum, the dependence of the spectrum upon the conditions of the experiment, the flame spectra, the spark spectra, the phosphorescence spectra, and absorption spectra.

The recent results of Crookes, and of Krüss and Nilson, are mentioned, but with the remark that the subject has not yet obtained the wide attention which it requires and merits.

In the quantitative part of the work electrolytic determinations are mentioned somewhat briefly, with a recommendation of thermo-batteries, or of Meidinger and Bunsen elements. We find no reference to gas analysis, which is now of growing importance.

The subject-matter of this work is of unquestionable value, but the language employed is not incapable of amendment. Thus we find the term "metalloids" constantly used. The element which we commonly, in virtue of priority, name "glucinium," is here termed "beryllium," and selenium and tellurium are made to rank as metals. In the very first sentence of the book we read:—"the analytical branch of the science is *given* a sharply-defined position." "Is given" and kindred expressions have come to be tolerated in newspaper paragraphs, but they are painful in a scientific treatise.

Continuity of the Colligative Properties and the Polymerisation of Matter through its Three Conditions. By JULIEN DELAITE. Brussels: F. Hayez. 1895.

THE author formulates the following law:—

"The density of a mixture of several solutions, having no chemical action upon each other, is, if the temperature remains constant, the sum of the densities of the component solutions, if we refer their density to the total volume and accept as true the law of Boyle-Mariotte applied to the dissolved salt."

He gives a table of all the atomic volumes, showing that the condensation is inversely as the chemical activity of the elements. Potassium, sodium, calcium, bromine, all very active substances, have low atomic coefficients, whilst the heavy metals and carbon are most strongly condensed. Diamond is said to have the strongest condensation, = 3271.

Another table gives the "integral weights" of the elements, not at all coincident with their atomic weights, and ranging from H=1 to Os=2498⁸⁰. Helium and argon do not appear to have come under the author's investigation. By combining the atomic coefficients and the integral weights, Dr. Delaite arranges the elements in eight series. He remarks that though carbon possesses the highest atomic coefficient, yet its integral weight is relatively low, which partly explains the great activity of this substance in organic compounds. He believes that the chemistry yet to be constituted will be better entitled than that of Sterry Hunt to the title of a "New Chemical System."

A New Bactericide.—German medical and hygienic papers are now discussing a new bactericide bearing the utterly misleading name of "argonine." We hasten to inform our readers that this novelty is not a compound or derivative of argon, with which it has not the remotest connection. It is a compound of silver and caseine.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxi., No. 13, September 23, 1895.

Specimen of Black Carbon from Brazil.—Henri Moissan.—This carbon is a variety of black diamond which sometimes exhibits a confused crystallisation, and sometimes presents a shagreeny aspect. M. des Cloizeau in his study on carbon has mentioned various crystals, among which is a complete cube with rounded edges. Such carbon is met chiefly in the province of Bahia and in small quantities in Borneo. It is much valued for tipping the crowns of boring apparatus. When of good quality its value is about 65 francs per carat. The sample which I have the honour of submitting to the Academy was found in the region between the Rio à Rancador and the brook das Bicas in the territory of the town of Lençoes. It weighs 630 grms. = 3073 carats, and is consequently the largest specimen which has been hitherto found. It is of a rounded form, distinctly black. On examination with a low microscopic power it has the appearance of a substance from which gases have escaped whilst in a pasty state. It is porous, and has lost about 19 grms. in weight since being taken out of the earth. The Brazilian miners have to pay to the owners of the lands on which they work a royalty of 25 per cent on the gross yield of stones and also a tax to the Government.

Composition of Pelageine.—Dr. A. B. Griffiths and C. Platt.—The authors have determined the chemical composition of the violet pigment of the Medusa (*Pelagia*). The pigment and fatty substances are soluble in boiling alcohol and ether. The filtered solution is evaporated to dryness; the residue is treated with a solution of soda, and the pigment rapidly extracted with carbon disulphide. On spontaneous evaporation the violet pigment is left as an amorphous residue. Of this pigment 0.2058 grm. yielded 0.47325 c.c. (?) of carbonic acid and 0.081 of water. 0.4605 of the pigment yield 15.15 c.c. of nitrogen at the barometric pressure of 742 m.m. and the temperature of 15°. The results answer to the formula $C_{20}H_{17}NO_7$. This pigment, which we name pelageine, is soluble in alcohol, ether, and acetic acid, insoluble in water, and very soluble in carbon disulphide. In an isolated state pelageine is bleached by light, and on spectroscopic examination it does not show any characteristic absorption-bands.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xiii.-xiv., No. 9, 1895.

Thermic Study of the Anhydrous Barium and Strontium Iodides.—M. Tassily.

Researches on the Combining-heats of Mercury with (other) Elements.—Raoul Varet.—A determination of combining-heat of mercury with iodine (= +24.7 cal.), bromine (= +40.7 cal.), oxygen (= +21.3 cal.), and chlorine (= +49.8 cal.).

Amorphous State of Melted Bodies.—C. Tanret.—Not all crystalline bodies re-crystallise on becoming solid after fusion. Some remain amorphous; and many, which crystallise under ordinary conditions, become amorphous if cooled abruptly. Among those which are thus rendered amorphous after fusion, the author mentions the pentacetines of glucose and the hexacetines of the active inosites.

Contribution to the Study of the Dissociation of Active Salts in Solution.—Ph. A. Guye and B. Rossi.—This voluminous paper is not adapted for useful abstraction, and does not merit insertion *in extenso*.

Calcium Phosphate in Milk.—L. Vaudin.

Isomeric States of Mercury Oxide.—Raoul Varet.

Volumetric Determination of Zinc.—L. Barthe.—A reply to the criticisms of H. Lescœur, who has operated upon a sample containing 13.9 per cent of impurities.

Preparation of Ethylamine by the Reduction of Ammonium Aldehyde.—Ferdinand Jean.—The author puts in a flask 10 grms. ammonium aldehyde, recently prepared, along with a little water and 20 grms. zinc powder. He then adds, in ten minutes, 150 grms. of hydrochloric acid (1 : 2), and after ten more minutes, 20 grms. concentrated hydrochloric acid, moderating the reaction by cooling the flask in a current of water. After forty-five minutes, it is heated for half an hour on the water bath. To obtain the ethylamine a large excess of soda is added so as to dissolve the zinc salt, and a violent current of steam is passed into the flask whilst heat is still applied.

Action of the Primary Aromatic Amines on the Non-symmetric Ketonic Compounds.—L. Simon.—This memoir is not adapted for useful abstraction.

Dimethylamido-a-caproic Acid.—E. Dunvillier.—Also not adapted for abstraction.

Propionic Ethylhydantoine (Ethyluraminodopropene).—E. Dunvillier.—Ethylamidopropionic acid yielding merely a hydantoine and not the corresponding hydantoic acid, and the amidic acids of the amines of the fatty series yielding merely a creatinine and rarely a creatine, the author is led to believe that the same amido-acids generally yield merely hydantoines.

Three Octochlorophenols.—Et. Barral.—These octochlorophenols possess certain identical properties which are also common to hexachlorophenol:—(1) Reduction to pentachlorophenol by tin and hydrochloric acid; (2) decomposition by heat into chlorine and products containing perchlorodioxypheylene; (3) formation of pentachlorophenol acetate with acetic anhydride. These isomeric octochlorophenols are much more stable than hexachlorophenol. They are perchloro-acetones, differing from hexachlorophenol by Cl_2 ; that is, *trichlorides of pentachloro-cyclo-hexa-diene-ones* in which the position of the three atoms of chlorine has yet to be determined.

Hexamethyleneamine. Action of Phenylhydrazin Hydrochlorate.—M. Delepine.—Here we have the total elimination of the typical hydrogen. Methylenephenylhydrazin, $CH_2CH_2=N-NH-C_6H_5$, which would correspond to the general formula of the phenylhydrazin aldehyds, still reacts upon formic aldehyd to yield trimethylene-diphenyldihydrazin.

Hexamethyleneamine Chloromercurates and Iodomercurate.—M. Delepine.—The author has obtained three chloromercurates and one iodomercurate, and considers it certain that by varying the conditions we may augment their number on account of the multiplicity of basic functions in the molecule.

Novel Reactions of Morphia.—G. Bruylants.—Already inserted.

Untrustworthiness of Cremometers for Determining the Fatty Matter in Pasteurised Milk.—P. Cazeneuve and E. Haddon.

Sterilisation of Milk, and on Lactic Fermentation. P. Cazeneuve.—The author's conclusions are:—1. If it is true that a heat of 110° (Pasteur, Hueppe) for half an hour is required to kill the lactic ferment, a temperature of 98° to 100° applied for an hour often destroys it, and in all cases attenuates it so far as to render it sterile in deoxygenated milk. As for the pathogenic ferments they are certainly destroyed. 2. In industry the apparatus which I have described permitting the complete immersion in boiling water of the sterilising bottles and the total deoxygenation of the milk and the containing vessel secures its indefinite preservation without any savour of rancidity and without coagulation. 3. Milk at 98–100° has

digestive properties, as demonstrated by clinical observation and experiment (Dr. Rodot), at least equal to those of raw milk, whilst it has the well known superiority of not being the vehicle of certain contagious microbia (Dr. Budin, &c.). It has the advantage over milk boiled at 110–120° of not turning yellow, and not taking a taste of burning or of peptone so frequently met with in milks sterilised at this temperature. 4. My observations have permitted me to establish that the lactic ferment appears little diffused in the air. Milk is chiefly contaminated by contact with impure objects.

Mordant of Glucina.—Maurice Prudhomme.—In preparing the mordant the author sets out with a crystalline glucinium sulphate, free from iron, and containing merely traces of alumina. 10 grms. of this sulphate were dissolved in 75 c.c. of distilled water, precipitated with ammonia, and pure ammonium carbonate is added to the solution. After twenty-four hours, it is filtered and heated in the water-bath to expel any excess of ammonium carbonate. The deposit of glucinium carbonate is redissolved in acetic acid and the mordant is made up to 100 c.c. The cloth worked in this bath is dried in the stove, aged for twenty-four hours in a moist atmosphere at about 35°, and duned in a dilute solution of ammonia at 60°. The swatches took a garnet shade corresponding to *violet-red* 1, 4/10 black of Chevreul's chromatic circle. The author concludes that glucina behaves as a protoxide and not as a sesquioxide from a tinctorial point of view.

MISCELLANEOUS.

Impurities in Milk.—The *Medical Press* of October 2nd quotes Dr. Buckhaus, of Berlin, that this city consumes in its milk-supply 3 cwts. of cow-dung. Whether this is the daily consumption of so unsavoury an addition we do not learn.

Diamonds.—According to the *Chemiker Zeitung* a diamondiferous rock has been discovered on the River Kamanka, in the Southern Ural. The diamonds are said to resemble those of Brazil, having a purer water than those of South Africa.

Discovery of Saltpetre at the Cape.—Attention has been called from time to time to the importance of searching for deposits of potassium salts in the Colonies and India. According to *South Africa* it appears that beds of earth rich in potassium nitrate have been discovered in the Cape Colony, and are now being worked on a practical scale. Samples have been found containing as much as 70 per cent of this valuable salt, but the average seems to range from 12 to 15 per cent. Of course the extent of the deposits has not yet been determined. The value of this discovery, if the supply is considerable, is beyond question.

Influence of the Presence of Lead Acetates on the Results of the Determination of Inverted Sugar by the Fehling-Soxhlet Method.—Arthur Bornträger.—The author confirms the statement of C. H. Gill, which appeared in a paper on the examination of glucose-containing sugars, read before the Chemical Society, March 16, 1871. Gill arrived at the conclusion that in presence of basic lead acetate, solutions of invert sugar seem to have a less reductive power than in the absence of the lead salt. Bornträger expresses his regret that he did not meet with Gill's original paper, but only imperfect, and to some extent misleading abstracts. — *Deutsche Zucker-Industrie*, August 9, 1895.

ERRATA.—The title of the paper by Messrs. Auden and Fowler (p. 163) should read "The Action of Nitric Oxide on Certain Salts," instead of "Nitric Acid." P. 124, Queen's College, Cork, for "Assistant—D. J. O'Mahony, F.C.S.," read "Demonstrator—R. E. Doran, F.C.S."

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THE CHEMICAL NEWS.

VOL. LXXII., No. 1873.

ON THE SENSITISING ACTION OF DYES ON GELATINOBROMIDE PLATES.*

(ABSTRACT).

By C. H. BOTHAMLEY, F.I.C., F.C.S.

ALTHOUGH many dyes have been examined since H. W. Vogel's discovery in 1873, very few of them exert any marked effect in making gelatinobromide plates sensitive to the less refrangible rays of the spectrum. Only cyanin and the dyes of the eosin group (including the rhodamines), with perhaps malachite-green, alizarin-blue, and chrysoidine, exert any practically useful effect.

The main points established by previous observers may be summarised as follows:—(1) all the dyes that act as sensitisers are readily affected by light when in contact with paper, fabrics, &c.; (2) in order that a dye may act as a sensitiser it must have the power of entering into intimate union with silver bromide, forming a kind of lake; and (3) it must show a strong absorption-band for the particular rays for which it is to sensitise. It is important to observe that the converse of these statements is not necessarily true, since several dyes that have all these properties show no appreciable sensitising action.

Experiments by Dr. E. Vogel on the rate of fading and the sensitising action of the eosin dyes, led him to the conclusion that the order of sensitising effect coincides with the order of fading when the dyes are exposed to light. The order in which he places the dyes does not, however, correspond with the order of fading as observed in dyed fabrics, and the experimental method that he used is open to criticism.

The author's observations on the fading of the various sensitisers when exposed to light in contact with gelatin alone, led him to the conclusion that, although all the sensitisers are readily affected by light, the order of sensitising effect does not necessarily correspond with the order of fading, whether the dyes belong to the same chemical group or not.

There are two chief hypotheses as to the mode in which the dyes act, namely, (1), the view held by Abney, that the dye itself is oxidised by the action of light, the oxidation product remaining in contact with the silver bromide; and when the plate is treated with the developer, the latter and the oxidation product, acting simultaneously on the silver bromide, bring about its reduction; and (2), the view first definitely formulated by Eder and endorsed by Vogel, namely, that the energy absorbed by the dyed silver bromide is partially used up in bringing about the chemical decomposition of the silver bromide, instead of being almost entirely converted into heat as when absorbed by the dye alone.

The author has found that the less refrangible rays will produce a photographic image on the sensitised gelatinobromide plates when they are immersed in powerful reducing solutions, such as a mixture of sodium sulphite and pyrogallol. This holds good for cyanin, the eosin dyes, the rhodamines, and quinoline-red, whether the sensitiser has been added to the emulsion or has been applied to the plate in the form of a bath. It is therefore impossible to attribute the sensitising effect to any intermediate oxidation of the dye.

Experiments with various reagents, such as potassium bromide, potassium dichromate, mercuric chloride, and

dilute hydrogen peroxide, seem to show that the chemical nature of the latent image produced by the less refrangible rays on the specially sensitised plates, is precisely the same as that of the latent image produced by the more refrangible rays in the ordinary way.

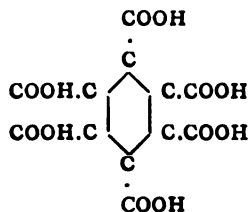
Further proof in the same direction is afforded by the fact that the effect of the sensitisers extends to the production of a visible effect by the prolonged action of light.

The balance of evidence is therefore greatly in favour of the view that the dye absorbs the particular groups of rays, and, in some way which is not at all clear, hands on the energy to the silver bromide with which it is intimately associated, and which is thereby decomposed.

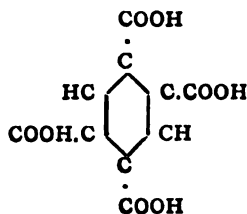
NOTE ON THE CONSTITUTION OF CAMPHORIC ACID.*

By J. J. SUDBOROUGH, D.Sc., Ph.D., F.I.C.,
Lecturer on Organic Chemistry, University College, Nottingham.

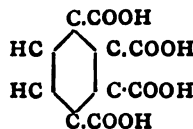
THE behaviour of camphoric acid on esterification (J. W. Brühl, *Ber.*, 1893, xxvi., 284) is very similar to that of some of the aromatic polycarboxylic acids investigated by V. Meyer and Sudborough (*Ber.*, 1894, xxvii., 3146). These authors have shown that a carboxylic group which has substituting groups in the two ortho-positions is incapable of yielding an ester under the usual treatment with alcohol and hydrogen chloride. Thus, mellitic acid—



gives no ester. Pyromellitic acid—

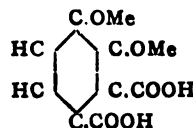


gives a neutral ester, $\text{C}_6\text{H}_2(\text{COOEt})_4$. And prehnitic acid—



gives a dialkyl ester, $\text{C}_6\text{H}_2(\text{COOH})_2(\text{COOEt})_2$.

Wegscheider (*Monatshft.*, 1895, xvi., 75) has since shown that hemipinic acid—



* Read before the British Association (Section B), Ipswich Meeting, 1895.

* Read before the British Association (Section B), Ipswich Meeting 1895.

which is a dicarboxylic acid, yields a mono-alkylic ester, and thus resembles camphoric acid very closely indeed.

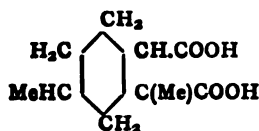
It is true of both hemipinic and camphoric acid that if the esterification is carried out for some time at the boiling-point of the alcohol, small quantities of the neutral esters are also formed; the main product, however, is always a mono-alkylic ester.

The reason for such behaviour is, beyond doubt, to be sought for in the stereo-chemistry of the molecule, the ortho-substituting groups hindering the action of the reagent which is employed.

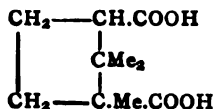
This view has received support from the recent investigations of V. Meyer on the esterification of many other aromatic acids, and also from those of the author on substituted benzoyl chlorides and benzamides (*Journ. Chem. Soc.*, 1895, 587 and 601). Whether we regard the substituting groups as filling up the space and thus preventing the formation of some intermediate additive compound, as Wegscheider suggests, or whether we regard them as simply preventing the entrance of the alkyl groups into the molecule, is of no importance in the present discussion.

We are thus, to some extent, justified in concluding that the characteristic behaviour of camphoric acid on esterification is due to stereo-chemical causes. Any constitutional formula proposed for the acid should therefore indicate stereo-chemical grounds for such behaviour.

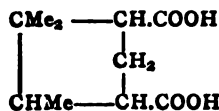
If we take three of the formulæ which have been more or less generally accepted, viz.—



Armstrong.



Bredt.



Tiemann.

we find that in no case have we a carboxylic group which has substituting groups in the two ortho-positions. In the formulæ of Armstrong and of Bredt, however, one carboxyl is ortho-substituted on the one side, and then has a methyl group attached to the same carbon atom to which it is united. It may be that this methyl group has a similar influence from a stereo-chemical point of view as a methyl group in the ortho position. If this is really so, then we can see sufficient grounds for the analogy between camphoric acid and hemipinic acid. If, however, we take the formula recently suggested by Tiemann (*Ber.*, 1895, xxviii., 1079) we see that both carboxylic groups are similarly situated; they both have substituting groups in one ortho position, but not in the other; and, further, neither has a substituting group attached to the same carbon atom to which it is united. We thus see no reason why one carboxyl should behave differently from the other on esterification. It must be pointed out that hemipinic, mellitic, and the other acids are all benzene derivatives, whereas camphoric acid, according to Armstrong, is a hexamethylene derivative, and according to Bredt and to Tiemann a pentamethylene derivative. J. van Loon has recently shown (*Ber.*, 1895, xxviii., 1270) that polycarboxylic acids of the hexamethylene series, e.g., hydromellitic and isohydromellitic acid, behave very similarly to the acids of the benzene series, except for the difference that is caused by cis- and trans-isomerism.

ON SOME STILBENE DERIVATIVES.*

By J. J. SUDBOROUGH, D.Sc., Ph.D., F.I.C.

THE author has prepared monochloro-, methyl-chloro-, and ethyl-chloro-stilbene by the action of phosphorus pentachloride on deoxybenzoin and on its methyl and ethyl derivatives. The monochloro-stilbene differs from that described by Zinin (*Annalen*, cxlix., 375), as it is a solid, which crystallises from alcohol in large colourless plates. It melts at 53°–54°, and yields additive compounds with bromine, with chlorine, and with "nitrous acid." These, together with the corresponding compounds obtained from methyl- and from ethyl-chloro-stilbene, are described. An oily monochloro-stilbene, corresponding to that of Zinin, has also been prepared, and is being subjected to further examination in order to determine whether it is merely an impure form of the crystalline compound or a true stereoisomeride.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 179).

To have the air motionless, at the same time, outside and inside a closed room, however large, is a condition so rare that almost all spectroscopists acknowledge that the sodium D line is *always* seen in a Bunsen burner or in a blowpipe fed with hydrogen.

When one has a chance of having the air relatively pure, the disturbance which one is obliged to make one's self in the room in order to work soon sullies the purity of the medium.

I have ascertained that the time suitable for the experiments themselves is very small; it is at the most an hour and a half a day; and it is only in the morning, from 9 to 11 o'clock, when the external air has been saturated with moisture for several days, that we can hope to find it at Brussels, on condition of having taken care to wash, with plenty of water, the floor and the walls of the room the previous evening, in order to rid one's self, so far as may be, from dust accumulations, of having admitted thither air saturated with moisture, of keeping the floor wet, of refraining from walking about the room, and of only being helped by a single assistant or a single witness. When the floor is dry and the air of the room is disturbed by walking about, or by draughts caused by the doors, by the window-shutters, and above all by the roof of the room, the pure deep blue colour characteristic of the flame of a Bunsen burner alters towards indigo, to become finally a distinct violet, and even reddish; one then often observes in it bright points which give a yellow light.

The prismatic analysis of the flame shows in it the existence of sodium and calcium in an intermittent or continuous manner, according to the magnitude of the disturbance of the air. The introduction of hydrochloric acid in this flame allows one to see the spectrum of calcium with great relative clearness.

In air disturbed by motion, the invisible flame of pure hydrogen, the blowpipe flame of hydrocarbon in air, or of oxyhydrogen, turns distinctly yellow, often even red, and becomes very bright. The colour and brightness of this flame increases with the magnitude of the disturbance.

The difficulties against which one has to strive whilst one is attempting to ascertain the truth of facts, do not include simply such impurities as the ordinary air may contain, but depend equally on the state of purity of the gases employed and of the apparatus through which one

* Read before the British Association (Section B), Ipswich Meeting, 1895.

passes them, or on the burner in which one completes the combustion of them.

It is essential that the illuminating gas, hydrogen, air, and oxygen which feed the blowpipes should themselves be entirely freed from suspended particles of sodium or calcium.

I have found that one of the best and surest methods of purifying illuminating gas, hydrogen, oxygen, and air from all suspended particles, is to let them pass through pure boiling water, and to pass them into and store them for at least twenty-four hours undisturbed in large gasometers, over water free from volatile bodies and made alkaline by lime or baryta.

When afterwards used they do not show any trace of the spectrum of sodium or calcium.

It is so difficult to deprive dry air in motion of suspended matter, that one distinctly notices the presence of sodium in the flame of a platinum or silver blowpipe when fed with hydrogen or purified illuminating gas, and either external or internal air supplied and purified by its passage through water-bellows or a water-pump. I have only succeeded in removing the sodium which is contained in insoluble suspended particles from the external or internal atmosphere, even with the assistance of a water-pump, by passing it through a metal heater containing pure boiling water.

Having regulated the supply of purified air and the boiling of the water, so as to obtain a supply of air and water vapour in nearly equal volumes, the condensation of steam, during its passage along a condenser of well-polished tin, ensures the deposit of such insoluble particles as may have survived the purification by the pump, and thus gives, when using either illuminating gas or pure hydrogen, a blowpipe flame in which spectrum analysis does not enable one to detect the sodium line, it being well understood that the air of the room or of a lofty and comparatively confined closet, with damp walls, in which one is working, is itself entirely freed from sodium particles.

The steam, when condensing, deposits with itself the insoluble matter suspended in the air supplied by the bellows or the pump.

I have tried an experiment, on a very large scale, for the purpose of ascertaining the weight of sodium particles thus eliminated. I worked during a moderate southerly breeze, on air taken from the street in which I live, running from east to west, 9 metres above the ground, which is about 50 metres above the surface of the river running through the town, and about 67 metres above sea-level. Whilst the apparatus was working I took pains to satisfy myself, by several repetitions, that after the condensation of steam the air mixed with it was completely free from sodium particles.

The condensed water, as it was formed, was passed through a double filter-paper that had been freed by a simple process from all traces of mineral matter, and held in a covered platinum funnel. I found that the combustion, in a closed vessel and at the lowest possible temperature, of the double filter, through which had passed *ten litres* of water after the pump had been working for sixteen hours, only left 0.00023 grm. of brown ferruginous ash,—that is to say, 23/10,000,000 of its weight, supposing, be it understood, that not a particle* of suspended matter had been retained in the well-polished tin condenser. The volume of air supplied by the pump to the distilling apparatus amounted to about 17 cubic metres.

In whatever manner the water was collected into a glass jar, it was impossible for me to detect in it, by spectrum analysis, the slightest sign of the sodium line. The water-pump, therefore, had robbed the air of its soluble compounds of sodium; on the other hand, the brownish ash, having been moistened with hydrochloric acid freshly prepared in the platinum dish, and introduced into an hydrogen flame on the end of a platinum

* A filter of good paper, treated successively with hydrochloric and hydrofluoric acids, left no trace of ash when burnt.

loop, at once coloured it a brilliant yellow, and with the spectroscope I recognised the presence of calcium and sodium.

The last remaining cause of the difficulties which one meets in spectrum analysis, when one attempts to solve important questions, rests in the apparatus used for producing the flames.

As regards platinum, experience has taught me that by melting and refining one rids it entirely of sodium. As a matter of fact I have never succeeded in detecting the appearance of the sodium line in platinum which has been purified by re-melting in the air in an oxyhydrogen blowpipe. I have noticed, on several occasions, that platinum which had been melted in a lime crucible, on being re-melted in an oxyhydrogen flame, gave temporarily a calcium spectrum. Whatever the reason might be, when made into either sheet or wire, the re-melting in air got rid of the calcium.

If platinum which has been kept for some time in air, even protected from dust, be put into the flame of a Bunsen burner or an hydrogen flame, it at once colours them yellow and shows the sodium line, but never a calcium spectrum, not even when moistened with hydrochloric acid. The fact that these flames turn yellow, first noticed by Messrs. Bunsen and Kirchhoff, is known by all spectroscopists. *This colour disappears when the metal is raised to a white heat.*

If platinum which has been lying in air, either in a room or outside, and unprotected from the dust, be put into the flame of a Bunsen burner or an hydrogen flame, it colours them yellow tinged with red: this colour lasts so long as the platinum has not been melted and refined in a lime crucible, or even if it has not been treated when warm with a mixture of hydrofluoric and hydrochloric acids diluted with their own weight of water. I have ascertained that the particles suspended in the air, both in the room and outside in the town of Brussels, which are insoluble in water, include, besides organic salts, silicates of alumina, calcium, iron, and sodium, carbonate of calcium, and silica. I have looked for potassium without being able to find it.

Experience has taught me that the tubes and fittings of platinum intended to be used in accurate spectroscopic researches ought to be kept protected from atmospheric dust, and before making use of them it is essential to give them a cleaning with dilute hydrofluoric and hydrochloric acids, and then with distilled water. I have ascertained as a fact that it is in the form of a fused silicate that the sodium remains on the surface of dusty platinum which has been raised to a white heat.

I have mentioned above that pure platinum, if kept some time in air and protected from dust, colours the flame of a Bunsen burner yellow, and gives the sodium line.

I tried some experiments to make sure of this fact, and found that pure platinum—either wire, sheet, or spongy—can be kept a great length of time in the damp open air, as well as in an air current issuing from a gasometer where it has been stored over water for twenty-four hours, and whence it issues saturated with water-vapour, without acquiring the power of colouring an hydrogen flame yellow, or giving the slightest trace of the sodium line.

It is the same with air purified by passing it through a metal boiler filled with boiling water, as I have explained above. This air is so completely free from sodium that not only can one leave platinum in it without contaminating it with sodium, but one can pass a spark from a powerful induction-coil through it, between platinum points or points of platinum covered with iridium free from soda, and still a spectrum analysis of the spark does not show the sodium lines among the atmospheric lines (see NOTE). This image can always be seen in the spark made in so-called pure air, even when hydrogen and illuminating gas can be burnt in it without showing the presence of sodium in the spectroscope. When describing

the spectroscopic study of lithium I shall return to this last fact.

(NOTE.—I made this experiment in an apparatus the details of which are known. It consisted, shortly, of a tube of hard colourless glass, 12 c.m. long, 8 c.m. internal diameter, and 10 c.m. external diameter.

A disc of hard glass, ground and polished on one side, 2 c.m. thick and 10 c.m. diameter, was fixed on either open end of the tube by means of clamps held together by metal rods with screwed ends. Each disc was pierced in the middle with a slightly conical hole, about 1 c.m. diameter, into which was carefully fitted a plug of pure silver, terminating outside in a small ring, meant for making contact either with the coil or the condenser. In the end of the conical silver plugs which pierced the discs was drilled a deep cylindrical hole $1\frac{1}{4}$ m.m. in diameter, and tapped, for screwing in one of the ends of a platinum rod of the same diameter, whose end was also screwed. To the other end of the platinum rod was attached a ball of the same metal, 3 m.m. in diameter, or a ball of platinum coated with pure iridium which had been fused on with the oxy-coal-gas blowpipe.

The distance between the platinum balls is adjusted by screwing the ends of the platinum rods more or less deeply into the screw holes in the silver plugs, which are kept in the discs by frictional grip. After some trials I varied this distance between 5 and 10 m.m.

In the middle of the space between the hole pierced in each disc and the inner surface of the tube is drilled a second hole, 6 m.m. in diameter, into which is fitted, by grinding with emery, a hard glass tap, so as to provide each disc with a tap for letting the air to be submitted to the electric discharge into the tube.

With the exception of the silver plugs and their extensions, the platinum rods and balls used as electrodes, the apparatus was made of hard glass, of which all the parts in mutual contact were ground and polished with emery, and kept pressed one against the other in such a manner as to form an air-tight chamber, and preserve by atmospheric pressure the air which was contained in it.

In order to rid the apparatus of all traces of free sodium compounds I made the following arrangements. After having washed the apparatus, short of its silver plugs, several times with pure water, I put it, whilst it was still wet, by means of the taps fitted to it, in communication with the gasometer containing the air which I wished to examine, and passed a rapid current of this air through it. I then adjusted the silver plugs and their extensions, the platinum rods and balls, which had just been washed, first with dilute hydrofluoric acid and then with pure water, which had been distilled and condensed into the platinum funnel.

The balls of pure platinum, or of platinum coated with pure iridium, having been first set to the required interval, and the apparatus having been fixed vertically in front of, and as near as possible to, the slit of the spectroscope, I passed alternately sparks and a brush discharge between the balls, whilst a current of the air under examination passed through the apparatus.

This current of air was supplied:—

1. By a gasometer in which the external air, washed simply by the pump, had remained for twenty-four hours over water made alkaline by baryta.
2. By a gasometer in which was received direct the air delivered by a water-pump into boiling water contained in a copper boiler surmounted by a chamber communicating with a tin refrigerator, which was kept at a low temperature by ice constantly renewed in order to condense the steam mixed with an almost equal volume of air from the pump.

When working in this manner, I observed that spectrum analysis, whether of the spark or brush discharge, however powerful they were, showed a spectrum *without* the double D line. With the spark long or short I ob-

served only the spectrum of atmospheric lines, and with the *strong* spark the spectrum of these latter lines, near to which appeared some *bright* lines, due either to platinum or iridium, according to the material of the surface of the balls used.

For this purpose I used in succession M. Hilger's direct-vision spectroscope, Steinheil's spectroscope, and lastly, M. Duboscq's large spectroscope with three prisms.

The absence of the yellow sodium line in the spectrum of the electric current passing through air saturated with moisture and purified by the methods described above, surprised the spectroscopists to whom I told my results. I will say in support of the perfect accuracy of this research, that during the revision of my spectroscopic studies with M. Depaire, we both decided, after several trials, that we could not see the yellow sodium line in the spectrum of a discharge passed through the partially saturated air in his spectroscopic laboratory.

Trying one day if we could obtain a compound of magnesium sufficiently free from sodium as not to show the sodium line on spectrum analysis of the spark through it, we not only ascertained the possibility of attaining this entire freedom, but we found also that the surrounding air, which fed the tube on which we were engaged, was free of sodium.

With the hope of being able to learn something of the nature of the substance which occasionally gave to the hydrogen made by water electrolysis, or by the decomposition of zinc or of zinc and lead by dilute sulphuric acid, the property of burning with a *ruddy yellow* flame, I filled the apparatus described above with hydrogen having this property, and whilst the current was passing through it I made a spectroscopic examination of the spark, weak or strong, passed through it.

I noticed that near the sodium line and the C and F hydrogen lines, the spectrum showed some faint lines, both red and distinctly green, grouped like nitrogen lines, and whose position coincided with that of nitrogen lines.

The presence of nitrogen is accounted for, since the hydrogen was collected and stored over aerated water.

Having replaced the gas with hydrogen deprived of the power of burning with a slightly visible flame, I proved by a spectroscopic examination of the spark through this gas the absence of the sodium line in the spectrum; but the presence, fully as noticeable, of the faint red and green lines seen in the gas endued with the property of burning with a visible flame.

The nature of the substance which, in certain conditions, gives hydrogen the property of burning with a ruddy flame remains to be discovered).

(To be continued).

CITRIC AND TARTARIC ACIDS FROM CANE-SUGAR.

(THIRD NOTE).

By Dr. T. L. PHIPSON.

ALTHOUGH I have not finished my investigations on this subject, I hasten to reply to those chemists who have not succeeded in obtaining the results alluded to in my former notes. It is easy to point out where their error lies, but it will perhaps not be so easy to get them to acknowledge it. They have failed to obtain the products by oxidation because they have not employed a sufficient quantity of permanganic acid. If they had jotted down the proportions requisite to supply the needful quantity of oxygen in order to convert cane-sugar to citric acid, they would have found that it requires at least as much permanganate as the weight of sugar employed. No lime precipitates of organic acids are obtained with small quantities, and hence the errors of observation alluded to.

These gentlemen all assert that the precipitate on boil-

ing consists of sulphate of lime with no trace of organic acid, and that when nitric acid is used instead of sulphuric acid to acidify the sugar solution, no precipitate is obtained.

Here is an experiment made without sulphuric acid, in which nitric acid alone was used:—

Equal weights of sugar, nitric acid, and permanganate of potash are taken, and the mixed solution is left for twenty-four hours in the cold. The clear solution is neutralised by carbonate of lime, which occasions a copious precipitate. The clear liquid from this precipitate, when boiled, yields a further smaller precipitate. The first contains tartaric acid, and perhaps saccharic acid, which has the same composition as citric acid. It is soluble without effervescence in acetic acid, and therefore contains no oxalic acid nor carbonic acid. The second precipitate is citrate of lime.

If the clear liquid, instead of being neutralised by carbonate of lime, is almost neutralised by carbonate of potash, and stirred with a glass rod whilst still acid, bitartrate of potash is precipitated. The liquid filtered from the lime salts contains the whole of the manganese.

The Casa Mia Laboratory, Putney,
October 10, 1895.

THE SEPARATION OF ARSENIC FROM OTHER ELEMENTS BY MEANS OF METHYLIC ALCOHOL AND HYDROCHLORIC ACID.

By CARL FRIEDHEIM and PAUL MICHAELIS.

THE method proposed by Schneider and almost simultaneously by Fyfe, subsequently repeatedly tested and modified,—i. e., to separate arsenic from other elements in the state of a volatile trichloride, by means of hydrochloric acid or sodium chloride and sulphuric acid,—has been re-modelled in a much more useful and generally applicable state by E. Fischer, who effects the distillation in certain conditions after the addition of ferrous chloride and hydrochloric acid. Hufschmidt, as also Classen and Ludwig, expedite the elimination of the arsenic in an extraordinary degree by the introduction of gaseous hydrochloric acid.

If this method is used for separating arsenic from other metals precipitable in an acid solution by means of sulphuretted hydrogen, the presence of ferric chloride at most presents the disadvantage that sulphur is carried down along with the sulphides. But if nickel, cobalt, and other elements of the ammonium sulphide group are present, their determination in the same specimen becomes very difficult, and that of iron impossible.

Also in the separation of arsenic from tungsten, vanadium, and molybdenum, in company with which it is found in numerous so-called complex combinations, the above-mentioned method would be as good as inapplicable. Tungsten would be in part separated out during the distillation, and have a disturbing influence. On the other hand, in consequence of the presence of the great quantity of ferrous chloride, it could scarcely be precipitated by concentration. The determination of vanadium by precipitation with mercurous nitrate would be rendered difficult by the simultaneous precipitation of mercurous chloride, and molybdenum could be separated from iron only by means of ammonium sulphide, which is neither accurate nor convenient.

In nearly all these and in numerous other cases we have found it preferable to substitute for ferrous chloride, methyl alcohol, because after distillation it leaves behind no fire-proof substance, but at most some carbon which is easily filtered or burnt off.

I. Behaviour of Arsenic Acid with Methyl Alcohol and Gaseous Hydrochloric Acid. *Modus operandi.*

Arsenic acid, on treatment with methyl alcohol and hydrochloric acid, is not esterified as such, but reduced to

arsen-trioxide, which then seems to evaporate in the form of its ester, a view supported by the circumstance that an anhydrous distillate is not precipitated by hydrogen sulphide unless decomposition has first been set up by the addition of water.

If the methyl alcohol solution of arsenic acid saturated with hydrochloric acid gas (0.2 to 0.3 grm. As_2O_3 , in 40 to 50 c.c. CH_3OH) is heated in a distillation flask on the water-bath, arsenical vapours are given off at 40° to 50° (thermometer in the flask), the main quantity following at 65° to 90°. A repetition of the operation yields only small quantities of arsenic, and on a third distillation the contents of the flask and the distillate are usually free from arsenic.

As the distillatory method it is convenient to use a round flask holding 250 c.c., which can be closed by means of a cap, ground to fit, and melted on to the condenser. Through this there passes (ground to fit) a dropping-funnel, which reaches almost to the bottom of the flask. The liquid distilling over flows into a flask of the capacity of about $\frac{1}{2}$ litre through a tube, ground in as a stopper and extending to the middle of the flask, and also ground to fit the outflow of the refrigerator. Laterally, on the neck of the flask, there is a ground junction for a three-ball receiver.

In carrying out the distillation we proceed as follows:—

The solution of the substance to be analysed is mixed in the distillatory flask with 50 c.c. methyl alcohol, as nearly anhydrous as possible, and, after the reception flask has been charged with 20 c.c. of concentrated nitric acid and the three-ball receiver with distilled water, the development of hydrochloric acid is introduced, in order to prevent the reflux of the methyl alcohol.

The dropping funnel certainly serves for the reception of the re-ascending methyl alcohol, but in some cases the liquid may spirt over into the dry bottle between the generating flask and the distillatory vessel, if the cock or the funnel is not closed soon enough. The distillation flask is kept cool by means of cold water, as otherwise the methyl alcohol might be heated to ebullition in consequence of the absorption of the hydrochloric gas. After complete saturation it is distilled off from a water-bath, whilst a very weak current of hydrochloric gas is kept up.

According to the quantity of the arsenic acid the distillation must be repeated once or twice, or even three times if the methyl alcohol has been diluted with much water. To this end the funnel cock is closed, the distillatory flask is refrigerated, the dropping funnel is filled with the corresponding quantity of alcohol, which is allowed to flow into the distillation flask.

When all the arsenic has passed over the contents of both receivers are transferred to a porcelain capsule holding 1 litre, and the receivers are rinsed out with water, covering the capsule with a clock-glass on account of the rather brisk development of gas. After the addition of 20 to 30 c.c. of concentrated nitric acid it is heated on the water-bath, keeping the capsule covered with a clock-glass until the violent escape of chlorine has come to an end. The liquid is then evaporated down to 100 c.c. After again adding an equal quantity of nitric acid, and complete evaporation, the residue is taken up with water, filtered, and precipitated with magnesia mixture.

II. Distillation of Pure Arsenic Acid.

Weighed portions of pure arsen-trioxide were oxidised to arsenic acid by means of concentrated nitric acid, the solution completely evaporated down, the residue mixed with water into the distillation flask, the water evaporated down to 5 to 10 c.c., and generally a threefold distillation is effected with 50, 40, 30 c.c. of methyl alcohol. The fourth distillate and the residue were always tested, and found free from arsenic.

III. Separation of Vanadic Acid and Arsenic Acid.

A direct separation of arsenic from vanadic acid has

hitherto been practicable only by reducing the latter to V_2O_3 by boiling with SO_2 , and precipitating the arsenic by sulphuretted hydrogen under pressure, re-oxidising the vanadium in the filtrate, and, according to the nature of the base present, separating with $HgNO_3$ or other agents, or titrating in the reduced solution with permanganate.

For the experiments we used ammonium vanadate, $AmVO_3$, repeatedly re-crystallised, and containing 77.82 per cent V_2O_5 , and pure arsenic acid.

On distilling $AmVO_3$ alone with methylic alcohol and hydrochloric acid, there passes over firstly a dark liquid containing vanadic acid. By degrees the distillate becomes lighter, and finally clear as water, whilst the colour of the liquid in the distillation flask changes from dark brown to a blue-green.

If 20 c.c. of water are added to the methylic alcohol only the first drops of the distillate have a violet colour. To prevent this the vanadic acid, before the addition of methylic alcohol, is reduced by heating with a little sulphurous acid, when the distillate is from the commencement clear as water, and contains no vanadic acid.

Before the second distillation of arsenic the water remaining in the flask is evaporated away as far as possible, since a volatilisation of vanadium is no longer to be dreaded.

In the following analyses the distillation was repeated four or five times, using at first 50 c.c. and afterwards 30 to 40 c.c. of methylic alcohol.

For determining the vanadic acid in the residue the contents of the flask were rinsed into a porcelain capsule by means of nitric acid, evaporated to dryness, transferred with ammonia into a weighed platinum capsule, and after evaporation and ignition the weight of the vanadic acid was determined.

IV. Separation of Arsenic and Molybdic Acids.

In the analysis of their alkaline compounds these arsenic and molybdic acids are generally separated by supersaturating the solution with ammonia and adding magnesia mixture. The precipitate of ammonium-magnesium arseniate thus obtained is allowed to stand for forty-eight hours, and filtered, dissolved in nitric acid, again precipitated with ammonia, and converted into magnesium pyroarseniate.

To the collected filtrates are added ammonium sulphide and sulphur, and the molybdenum sulphide precipitated by acid is converted into disulphide or metal by reduction in a current of hydrogen.

Though this method, on account of the ready entrance of molybdic acid into the double magnesium salt, does not give the most accurate results, it is still preferable to an indirect method in which both acids are precipitated together as mercury salts and ignited in a current of hydrogen. The arsenic then escapes and the molybdic acid is reduced to metal, but a part of the molybdenum is apt to be volatilised, and, on the other hand, its complete reduction is difficult to effect.

The authors' experiments were made with ammonium paramolybdate, three times re-crystallised, containing 81.55 per cent MoO_3 .

This salt, on distillation with anhydrous methylic alcohol and hydrochloric acid, behaves similarly to ammonium vanadate, but an addition of water is here sufficient to prevent molybdenum from passing over.

For the management of the distillation everything holds good which has been said concerning vanadic acid. The determination of the molybdic acid in the residue is effected in the manner described for vanadic acid. But the temperature must not be raised to redness. Hence the residue of evaporation is dissolved in ammonia and filtered into the platinum capsule, in order to remove the carbonaceous matter derived from the alcohol.

V. Determination of Arsenic Acid and Tungstic Acid.

The separation of arsenic acid from tungstic acid involves the greatest difficulties, as the former cannot be

entirely removed by ordinary precipitants, nor even by sulphuretted hydrogen under pressure.

It is best to follow Kohmann's directions, boiling the salt in question for half an hour with the double calculated weight of soda-lye, in order to split up the two components, and then with twice as much ammonium chloride as is necessary to combine with the alkali present; $\frac{1}{2}$ vol. of ammonia and magnesia mixture are added: the mixture is filtered after the lapse of two hours, washed with a mixture of ammonia and ammonium nitrate, and the precipitation is several times repeated. Certainly the total quantity of the tungstic acid can scarcely be separated from the ammonium-magnesium arseniate.

The collected filtrates are evaporated down with hydrochloric acid when the quantity of magnesium salt has a very disturbing effect.

We succeeded in the following manner in separating both acids with great accuracy:—

The principle of the method is that we determine in one portion of the substance the joint weight of both acids, and in a second the weight of the tungstic acid alone, and calculate the arsenic acid from the difference.

As we find, the determination of the total weight can be thus accurately effected:—The aqueous solution of the arsenic tungstate is heated on the water-bath, and whilst diligently stirring a solution of mercurous nitrate is added until no further precipitation takes place, whereupon the free nitric acid is neutralised by pure mercuric oxide suspended in water. After heating the whole (still covered with a clock-glass) for twenty minutes on the water-bath, it is allowed to cool, the precipitate is filtered off, washed with water containing nitric acid, dried, removed from the filter as completely as possible, and the rest still adhering to the paper is dissolved into a platinum crucible with warm dilute nitric acid. After evaporating away the acid the bulk of the precipitate is introduced into the crucible, covered with a large quantity (15 to 20 grms.) of weighed, anhydrous, normal sodium tungstate; the crucible is filled with water and evaporated to dryness on the water-bath, whereby the precipitate is intimately pervaded by the sodium tungstate.

The covered crucible is then gradually heated to 200° in the air-bath—whereby the rest of the water escapes—and cautiously ignited (under the draught-hood), first with a single burner, and then with a sixfold burner. A constant weight is obtained after a single ignition for half an hour.

The filter, to which a small quantity of tungstic acid still adheres, is burnt separately.

For determining tungstic acid alone, the precipitation and drying of the precipitate are effected exactly in the same manner, but, after its removal from the filter, the latter is burnt at once without a previous treatment with nitric acid; the main quantity of the precipitate is added, and ignited at once with the addition of the normal sodium tungstate.

The results obtained possess an exactitude which is not even remotely approached by any other method of determination. The analyses are also convenient and expeditious in execution, and gain further in simplicity if, in determining the tungstic acid, we use the Gooch crucible and thus dispense with the incineration of the filter.

The above method of the distillation of arsenic with methylic alcohol in hydrochloric acid is available also for the separation of arsenic from many other elements, especially from iron, cobalt, nickel, and copper, which it accompanies in numerous minerals.—*Berichte*, xxviii., p. 1414.

Synthesis by means of Cyanacetic Ether. — T. Klobb.—In this manner the author has obtained the phenacylcyanacetic and phenacylacetic acids and the methyl-methyl phenacylcyanacetate and the analogous ethyl compound. He has also studied the action of chloracetone upon sodium cyanacetic ether.—*Comptes Rendus*, No. 14.

THE SCIENCE OF EXAMINING.

By PETER T. AUSTEN, Ph.D., F.C.S.

MUCH severe criticism is being directed against examinations and much of it is timely and fully deserved. And yet when the criticisms are carefully considered they appear to be directed not so much against examinations as a method in education as against certain forms of examinations which are very prevalent and which certainly do not show anything more than evanescent memorisation, adroitness, or trickiness on the part of the student. No one will deny, however, that much of actual life is a kind of examination, and that we are being continually pressed to solve problems of all kinds, apply knowledge, and in general to act, and that on the success of our efforts will depend the positions we will attain, or at least maintain. There seems to be no reason why examinations should not be made an extremely important part of education, instead of being, as I fear they often are, an unmitigated nuisance to both student and teacher, a bone for the pedagogical critics continually to snarl over, and, when all is done, to be of no real use to either teacher or student, and to show nothing as to the real nature of the teaching done and the mental development of the student.

For the teacher who teaches from love of teaching, and who knows that successful teaching calls for the application of psychological principles far more than is generally supposed, there is a peculiar fascination in an examination paper. An examination may be made a test of the contents, capacity, quality, and action of a mind under defined conditions; but the paper must be a good one; I do not refer to the work of an inexperienced hand. The idea seems to be prevalent that anyone can write an examination paper. This is a great mistake. The elaboration of a paper that will really test not only the contents of the mind, but also its different functions as developed by a particular study under the guidance of a particular teacher, requires experience and ability. It is true that a man may be a good teacher and a poor examiner, but this usually arises from a lack of attention to the science and art of examining. My experience in this branch of pedagogical science leads me to believe that there are not very many really good examiners, and that the average examinations do not test the minds of the students as they ought to be tested. The average examination calls mainly for an exercise of memory, and for some proof that the student understands the matter he has studied. No man values the faculty of memory more highly than I do, or requires a better understanding of a given subject. But memory and mere understanding are only the foundations of education. More than this is called for. Some examinations require skill in observation, others accurate definition; while others bristle with problems. Some call for knowledge in which the teacher is weak. Almost every pedagogic earmark may be found in examination papers, but rarely is the paper constructed on such a plan that it tests not only the quality and quantity of knowledge in the mind, but also the various workings of the mind, and ascertains what the mind can do when set in action by the particular subject.

In my own speciality of chemistry there is an excellent opportunity for examination papers which may test the mind qualitatively and quantitatively, and probe both absorptive and productive powers. I have always taken a great interest in working out examination papers and in studying the minds as they appear in the answers. I am accustomed to work out questions under various heads. The following example will serve to indicate my meaning, and may also encourage others to experiment in examination science; and I think that the method will be found so interesting that the investigation will not be hastily dropped. I should add that in the examination paper as given to the students the questions are mixed up, so that the classifications given as follows do not appear.

Questions for Testing:—

Memory.—(1) Give a brief history of oxygen. (2) Outline the theory of phlogiston. (3) What are "copperas," "bluestone," "tincal"?

Accuracy of Definition.—(4) State concisely the laws of Dalton, Charles, Mariotte, and Avogadro. (5) Define a mechanical mixture. (6) Define an element.

*Observation of Experimentally Demonstrated Facts.**—(7) Describe and sketch an apparatus for producing acetylene from calcium carbide, and explain the working of it. (8) Describe and sketch the combustion of nitric acid in iodohydric acid.

Accuracy of Detail.—(9) Explain with the aid of sketches the reduction of hot cupric oxide by hydrogen, heating the oxide in a combustion-furnace and preparing the hydrogen in a Kipp generator.† (10) Make a sketch of a section of Pepy gasometer, and explain how the apparatus works.

Acquaintance with the Properties of Matter.—(11) Describe the properties and chemical behaviour of nitrogen, sulphur, zinc, silica, and iodine.

Retention of Oral Instruction.—(12) Explain the contamination of water by sewage. (13) Describe the process for making open hearth steel.

The Faculty of Comparison.—(14) State similarities and differences between the properties of oxygen and hydrogen. (15) What substances resemble lead sulphide in colour and solubility in nitric acid?

Lucidity of Statement.—(16) Describe minutely and without sketches the apparatus and method of preparing phosphine. (17) Prove by analysis of stibine by volume that the molecule of antimony is tetraatomic.

Recognition of Substances.—(18) A yellowish green gas with a suffocating odour. What may it be? (19) A colourless gas, very soluble in water, gives white fumes with hydrochloric acid. What may it be? (20) A white powder, insoluble in water; heated with concentrated nitric acid it evolves red fumes and yields a solution, which, when excess of acid is evaporated off, and it is diluted with water, yields a precipitate which is insoluble in concentrated nitric acid. What may this white substance be? (21) A chemist wishes to fill a jar with red liquid. What substance may he use?

The Ability to Observe.—(22) Give four examples of chemical change which you observe in this room. (23) Describe an ordinary red building-brick, stating dimensions and properties of surface, weight, fracture, &c. (24) Water expands on freezing. Give five examples of results caused by this expansion which you have personally observed.

The Application of Facts to Proofs.—(25) Prove that water is formed by the combustion of a kerosene lamp. (26) Prove that hydrogen sulphide contains sulphur.

The Interpretation of Phenomena.—(27) A piece of white paper on being held for an instant in the flame of a candle and at right angles to it, a black ring is formed on the paper. Explain what the ring indicates, and how the particles of carbon are formed, and why they are deposited on the paper. (28) A Roman candle on being ignited and then thrust under water continues to burn. How can this be accounted for? (29) Why cannot fish live in lakes on the tops of very high mountains?‡

The Application of Knowledge.—(30) The iodine falls into the sand box. How can the iodine and sand be separated? (31) A mixture consists of barium carbonate, sodium sulphate, and sulphur. How can they be separated? (32) A manufacturer has a waste product consisting of a liquid containing 40 per cent of sulphuric acid, 10 per cent sodium sulphate, and 5 per cent ferric sulphate. How can he treat it so as to convert it into other products that have commercial value?

* Given in lectures and not in text-book.

† Given in text-book and demonstrated in lecture.

‡ Compare London University Matriculation Examinations, Stoker and Hooper, p. 31. Q. 6.

Deceptive or Misleading Questions.—(33) Dilute sulphuric acid is poured upon zinc. A gas with a slight bluish* colour is evolved, which burns with a red* flame. What is it? (34) Chlorine gas is collected in a jar over mercury† in the usual manner. It is then brought into a eudiometer, mixed with twice‡ its volume of hydrogen, and exploded. How many volumes of hydrochloric acid gas will be produced?

The Imagination.—(35) Filthy water of the gutter, warmed by the sun's rays, escapes from a foul environment, and, condensing, sparkles like diamonds on the petal of the violet. Use this as basis for an allegory in life.

These questions do not by any means represent all the possible divisions of mental action, and I have purposely avoided those of a very technical nature, most of which, however, would fall under the heads given; but they will serve to indicate what opportunities there are to construct examination papers that shall test a student's knowledge and the working of his mind. It may be urged against the questions I have given that several of them might fall as well under one head as another, or that a few more elaborate questions could be made out and each question marked under the several heads. My experience, however, has not been that the real ends are best attained in this way. The question that is distinguished by its definite nature and object gets a clearer answer and gives a more satisfactory insight into the student's mental equipment and action than a long or complicated one. If, after teaching a student a subject for a certain time, an examination shows that he can bring forth nothing more than that which has been put into him, it may be inferred either that the teacher is incompetent, or that the student is intellectually deficient; assuming, of course, that the system in the particular institution permits the teacher to do his best, does not assign him more pupils than one man can teach, and requires the student to do the work assigned to him. In such case I think that the fault usually lies with the teacher. Still I admit that there are institutions in which educational work of a high pedagogical order is impossible, and mind development, as distinguished from mind cramming, is out of the question. In such a case students are produced who are saturated with knowledge, but who are incapable of utilising it. Like water-logged vessels they roll about aimlessly, and are unable even to keep out of the way of craft which are taking the fullest advantage of wind and tide. In such an institution the earnest teacher, when he fails, deserves sympathy more than blame.

The results of examinations, conducted on some plan like the one I have attempted to describe, are very interesting. Such examination papers are far more difficult to write than the calls for mere memorisation that are so frequently made on the student, and which a hasty cram will enable a fairly bright candidate to pass. The answers are more difficult to rate; and often an attempt to mark them according to the usual rules is unsatisfactory. It is quite easy to assign a mark to the amount that a student knows, or even to discriminate as to the quality of his knowledge. To assign a figure to his ability to apply this knowledge, to originate, to create, to act under its instigation, is more difficult; yet it can be done with a fair degree of success.

It must always be borne in mind that a man's value in this life does not depend merely on what he knows, but upon what he can do. *Ceteris paribus*, the more he knows, the more he should be able to do; for so much the greater should be the incentive, if the knowledge imparted to him acts on him as it should. Until technical education was introduced, this fact was not well understood, and it is still far from appreciated in many schools.

For instance: A shows in his paper an encyclopædic

* Colourless.

† Chlorine cannot be collected over mercury.

‡ Once.

knowledge. In his answer to Q. 11 he recites with great precision the properties of silica and iodine. But he fails to answer Q. 30, which calls for a conclusion dependent upon this knowledge. He is like a recruit who has been given a gun, but has not been taught how to fire it off. Such a student demands the teacher's attention at once. His mental inaction is usually the result of poor teaching.

It may not be amiss for me to say parenthetically here that teaching is the most difficult of all professions. It is not usually regarded so, but I believe that it is. Much of what is called teaching is nothing more than a kind of pumping. Knowledge is forced in through the most convenient intellectual orifice, a great deal being lost *in transitu*, and not a little leaking out afterwards. The engorged recipient is like a boiler whose feed-pump is too big for it and will not cease pumping, but fills the boiler entirely full of water and leaves no space for steam; whereon the engine slows down and stops, or throbs soggly with its cylinder filled with lukewarm water instead of hot expansive steam.

Again, a student may fail in his attempts to state anything correctly or exactly; but he fills pages with attempts to apply his knowledge, suggesting all sorts of ideas and applications. Most of them may be impossible, some even ridiculous. But no matter, let the teacher take hold of this boy at once, for the mind of an Edison, a Siemens, or an Ericsson may be seeking nourishment and development. Happy is the teacher who can discern what mean the instinctive strugglings of the embryonic master mind, and who can liberate it from the thralldom of routine—who can guide its first weak attempts to walk and climb, until it becomes hardy and venturesome, and fearlessly scales cliffs heretofore inaccessible: and so clambering by hitherto unknown ways to the peak discovers new fields for human activity, and cuts a wide path by which thousands may enter and take possession.

What man gets closer to the Creator than the teacher, who can discern and understand His idea as shown in the youth and who clears away the obstacles in the way of its development, nourishes it until it is strong and independent, and itself becomes creative? Verily such a teacher has his reward.

Examination papers constructed on the basis I have suggested, viz., to test not only the knowledge possessed by the student, but also the working of his mind upon the particular subject, will show more clearly the nature and condition of a mind than the daily recitation, because the case is more capable of systematic study and can be made to cover larger fields of mental activity. While I do not intend to suggest that such examinations should replace the regular recitation, I believe that they should be held frequently, and should serve a far wider purpose than that of merely noting the quantity of knowledge absorbed by the mind. Such an examination is not a mere matter of testing and registering; it is a creative exercise of the mind.—*Science*.

THE PRECIPITATION AND GRAVIMETRIC DETERMINATION OF CARBON DIOXIDE.*

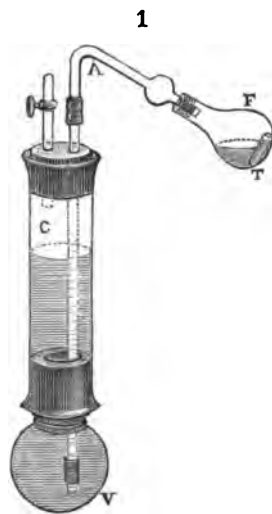
By F. A. GOOCH and I. K. PHELPS.

THE method upon which reliance is most confidently placed for the determination of carbon dioxide in solid carbonates, involving as it does the liberation of that gas by the action of a strong acid and its absorption in weighed potash bulbs, demands as conditions of the attainment of good results the careful observance of precautions and the expenditure of much time and attention. In the method described below we have sought to secure equal accuracy with greater economy of time and care.

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. 1, Aug., 1895.

Our plan is to effect the rapid absorption of the carbon dioxide, evolved by the action of acids upon carbonates, in barium hydroxide contained in a specially devised apparatus, to filter and wash the precipitated barium carbonate under a protecting layer of xylene, to dissolve in hydrochloric acid the washed carbonate upon the filter or adhering to the receiver, to convert the barium chloride thus obtained into the form of the sulphate, and from the weight of the last to calculate the carbon dioxide originally liberated by acid from the carbonate.

The apparatus which we use, and which is shown in the figure, consists of a flask for the evolution of the carbon dioxide, properly connected with a receiver in which the gas is retained until absorption is perfect. It is a form of a similar device employed by one of us (*Amer. Chem. Journ.*, i., 450) for the absorption of ammonia in hydrochloric acid and the complete retention of the ammonium salt thus formed, but so modified as to avoid the danger of diffusion of carbon dioxide through the rubber balloon—a source of error which we have found by experiment to be considerable when large amounts of the gas are handled.



The evolution flask (F) has a capacity of about 50 c.m.³, and is fitted with a rubber stopper through which passes a tube (A) wide enough (about 0.7 c.m. in interior diameter) to prevent the formation of bubbles, and expanded just above the stopper to a small bulb. The absorption cylinder consists of a wide glass tube (C), fitted at either end with a rubber stopper. The stopper at the lower end of the cylinder, placed vertically, carries a short tube, about 1.5 c.m. in diameter, to which is secured a smaller rubber balloon. The cylinder and balloon together hold about 100 c.m.³. The upper stopper is perforated with two holes, through one of which passes the tube of a glass stopcock, while through the other hole passes a long tube reaching to the interior of the balloon and provided with a valve (V)—preferably a modified Bunsen valve, of the pattern recently devised by Kreider (*Am. Journ. Sci.*, i., p. 132).

In using this apparatus a saturated solution of barium hydroxide (which is made hot, filtered into a syphon-bottle, and preserved from atmospheric action by a floating layer of kerosene) is introduced by pressure upon the air in the syphon-bottle or by suction applied to the stopcock of the cylinder. Such a solution contains about 5 per cent of its weight of the hydroxide, and we find it best to use in every case an amount at least a fourth in excess of the quantity theoretically required to absorb the carbon

dioxide, and to fill the cylinder and balloon nearly full of liquid. The carbonate is weighed, introduced into the flask, and washed down with 15 or 20 c.c. of boiled water, which is protected in the wash-bottle from carbon dioxide in the breath by a balloon attached to the inlet tube. A small tube, holding enough hydrochloric acid to effect the decomposition of the carbonate to be analysed, is placed in upright position in the evolution flask. The stopper is inserted in the flask, and connections are made as shown in the figure; the little tube containing the acid is overturned by inclining the flask; the acid mixes with the water, and effervescence begins. Heat is applied, and the liquid in the flask is boiled until that in the cylinder is heated by the steam nearly to the boiling-point, in order that the precipitated barium carbonate may become as granular as possible. The carbon dioxide evolved and the air in the flask are transferred in the process to the absorption cylinder, the valve serving to prevent the back flow of the liquid, while the balloon expands to give room to the air and condensed steam. When the boiling is done the flask and tube are disconnected at the rubber joint, the cylinder is shaken to insure the absorption of the carbon dioxide, and the liquid carrying the greater part of the precipitate is transferred through the stopcock to a filter carefully fitted to its funnel, moistened with water, and containing about 5 c.m.³ of xylene (which we found to be preferable to benzene, kerosene, or amyl alcohol), the function of which is to rise to the surface when the aqueous solution is added, so as to protect the barium hydroxide from the action of the carbon dioxide of the air. By manipulating the balloon and the stopcock (to which a little funnel may be attached by a piece of rubber tubing for convenience in introducing wash-water) the cylinder may be emptied and washed out with hot boiled water, though, of course, a very considerable portion of the precipitate remains adhering to the walls of the absorption apparatus.

We prefer to prepare the filter for use with the suction pump, but in the early stages of filtration and washing very little suction should be applied. When the barium hydroxide has been nearly washed out of the precipitate, the xylene is dissolved in a little hot alcohol, the suction is applied, and the washing is completed with hot water. The emulsion of xylene and water found in the filtrate is readily cleared up by alcohol. Finally, the barium carbonate in the absorption apparatus and upon the filter is dissolved in hydrochloric acid and precipitated in hot solution by sulphuric acid; the resulting barium sulphate is filtered, washed, and ignited upon asbestos in a perforated crucible, and from its weight the carbon dioxide which originally precipitated the barium, now in the form of the sulphate, is calculated. The results of a series of determinations made in this manner are recorded in the following table:—

(Ba = 137.43, S = 32.06, O = 16, C = 12.)

CaCO ₃ taken. Grm.	BaSO ₄ found. Grm.	CO ₂ actually present. Grm.	CO ₂ calculated. Grm.	Error in CO ₂ . Grm.
0.0500	0.1180	0.0220	0.0222	0.0002 +
0.0500	0.1183	0.0220	0.0223	0.0003 +
0.1000	0.2329	0.0440	0.0439	0.0001 -
1.1000	0.2347	0.0440	0.0442	0.0002 +
0.2000	0.4660	0.0880	0.0878	0.0002 -
0.2000	0.4653	0.0880	0.0876	0.0004 -
0.5000	1.1650	0.2200	0.2196	0.0004 -
0.5000	1.1657	0.2200	0.2197	0.0003 -
1.0000	2.3323	0.4400	0.4396	0.0004 -
1.0000	2.3309	0.4400	0.4394	0.0006 -

Various modifications of method and manipulation were put to the test of experiment, but the process which we have described has proved on the whole the most satisfactory. It is fairly rapid and accurate.

ON THE VAPOUR-TENSIONS OF MIXTURES OF VOLATILE LIQUIDS.*

By C. E. LINEBARGER.

(Continued from p. 184).

Choice and Purification of Liquids.

As stated previously, the liquids employed in the course of this investigation were those recognised to be strictly normal; and of those only such were chosen as can be gotten in a state of great purity. The only associated liquid taken was acetic acid, whose degree of association as well as whose physical properties are to a certain extent known.

An associated liquid was investigated for the purpose of applying the regularities and "normalities" discovered in mixture of normal liquids to mixtures of a normal liquid with an associated liquid. Great pains were taken to purify the liquids in the highest possible degree, it being the testimony of all those who have occupied themselves with experimental work on the vapour-tensions of liquids that even very slight impurities have a remarkably disturbing effect upon the accuracy of results; this is especially the case in results obtained by the static method; in the method employed by me, the influence of a slight amount of impurity is not so marked; still, for all that, it has been thought best to employ such material as had been most thoroughly purified.

In order that the readers of this paper may judge for themselves the degree of purity of the liquids examined, a somewhat detailed account of the method of purification of each liquid is given together with a statement of certain characteristic physical properties of each. All of the liquids, it may be stated beforehand, were bought as chemically pure from the dealers (Poulenc Frères, Paris, and Billault, Paris), and at least one pound—generally two or three pounds—subjected to the purifying operations.

Benzene.—Nearly three pounds of benzene—labelled chemically pure and free from thiophene—were treated a half-dozen times with sulphuric acid to remove last traces of the sulphur compound. The liquid was then repeatedly fractionally crystallised until about a pound was obtained melting at 5.3°. This purified product when partially solidified showed, no matter what the proportion of liquid and solid was, the same melting point. The whole was then distilled over a few pieces of sodium, no variation from the boiling-point 80.1° under a pressure of 756 m.m. of mercury being observed. Its specific gravity at 25° referred to water at the same temperature was found to be 0.876611.

Toluene.—Of the quantity of toluene taken for purification (about two pounds) more than four-fifths distilled at 109.8° to 110.1°, an indication that the commercial article was nearly pure. After a couple of distillations over a little sodium, more than a pound was obtained boiling constantly at 110.1° under a pressure of 758 m.m. of mercury. Its density at 25° referred to water at 25° was ascertained to be 0.86288.

Monochlorobenzene.—A couple of pounds of monochlorobenzene were repeatedly distilled in fractions until a constant boiling product resulted. About three-quarters of a pound were obtained, boiling at 131.8° to 131.9° under a pressure of 757 m.m. of mercury, and having a density of 25° (referred to water at same temperature) of 1.10362.

Monobromobenzene.—Nearly a pound of bromobenzene was fractionally distilled until a distillate was obtained boiling between narrow limits. About 150 grms. of the product, boiling at 154.3° to 154.5° under a pressure of 761 m.m. of mercury were obtained. The density at 25° referred to water at 25° was 1.49852.

Nitrobenzene.—The commercial article was repeatedly

crystallised until an almost colourless liquid was obtained, which, when solidified, showed the same temperature during the re-melting. It possessed a melting-point of 3.6°, and its density was 1.20201—

$$\left(\frac{25^\circ}{25^\circ}\right).$$

Chloroform.—About two pounds of "chloroform anesthétique" of commerce were washed a dozen times with water, dried thoroughly by means of fused calcium chloride, and distilled. The larger distillate boiled at 60.8° to 61.0° under a pressure of 751 m.m. of mercury; and, finally, nearly a pound was obtained boiling at 60.9° under a pressure of 755 m.m. of mercury.

Carbon Tetrachloride.—Two pounds were washed with water, and thoroughly dried by means of concentrated sulphuric acid. The product was then redified, and nearly a pound boiling throughout the operation at 76.6° under a pressure of 756 m.m. of mercury taken for the preparation of the mixtures. The specific gravity of this product at 25° referred to water at the same temperature was 1.58828.

Acetic Acid.—Two pounds of glacial acetic acid were repeatedly fractionally crystallised until a portion melting at 16.7° was obtained. The bottle containing it, as well as the mixtures made from it, were kept under an air-tight bell-jar by the side of very strong sulphuric acid.

Preparation of the Mixtures.

The mixtures were prepared by weighing out to a milligram, on a balance turning with a tenth m.grm. the liquids in a flask; the corked flask was tared, the less volatile liquid poured in and weighed, and then the more volatile. As from 40 to 100 grms. of the mixture were weighed out, the composition of the mixture was thus known to a ten-thousandth at least. The mixtures were preserved in bottles or flasks fitted with the finest corks, and kept in a dry cool dark closet. As, almost invariably, the necessary vapour-tensions of a liquid were made immediately after its preparation, no change of concentration occurred even with the most volatile liquids employed.

In the case of some of the mixtures of benzene and carbon tetrachloride, the residues of the investigated mixtures were united, and the amount of chlorine in the resulting mixture determined according to Carius's method.

The mixtures of benzene or toluene with acetic acid had their concentration controlled by an analysis. 5 to 10 c.c. of the mixture were carefully weighed out in a glass-stoppered flask, water was added, which took practically all the acetic acid from the benzene, and then standardised baryta-water run in to point of neutralisation. In no case did the analysis give results sensibly different from those calculated from the direct weighings.

(To be continued).

NOTICES OF BOOKS.

Elements of Modern Chemistry. By CHARLES ADOLPHE WURTZ. Fifth American Edition, Revised and Enlarged. By W. H. GREENE, M.D., and H. F. KELLER, Ph.D. (Strassburg). With a Portrait of the Author and numerous Illustrations. Philadelphia and London: J. B. Lippincott Company. 1895. Pp. 808.

In examining this work, we have firstly to consider the original as it issued from the pen of the late illustrious Prof. Wurtz, and secondly the version executed by Messrs. Greene and Keller.

The original must be recognised as an admirable summary of chemical science down to the death of the author (1884). Though it was more especially adapted to the requirements of medical students, it may be recommended as one of the best elementary works on chemistry of a

* Abridged from the *Journal of the American Chemical Society*, vol. xvii., No. 8, August, 1895.

moderate compass. Professor Wurtz does not discuss the nature and possible origin of the elements; he gives them his provisional acceptance without speculating on their possible ultimate nature. Hence Prout's hypothesis is ignored, and the periodic classification of the elements with its consequences is ascribed exclusively to Mendeleeff, without any reference to Lothar Meyer or Newlands.

As many discoveries of the highest importance have been effected within the last twelve years, the task of the translators has not been easy. They have added notices of the isolation of fluorine, of argon and helium, of hydrazine, hydrazoic acid, and their principal derivatives, of stereoisomerism, and of some of the more recent discoveries in the chemistry of the rare earths. The localities occasionally given, e.g., for the occurrence of mineral waters, are almost exclusively American and little known to European readers. The language employed is not in all cases idiomatic English as spoken to the east of the Atlantic, but a moment's reflection enables the reader to detect the meaning.

The work before us deserves an honourable position in the library of the chemical student.

On Dangers to Men Employed in Chemical Works, Means of Preventing Accidents, and Conditions of Work. A Critical Discussion of English and German Industrial Relations, occasioned by the English Parliamentary Report of 1893. ("Ueber Gefahren für die Arbeiter in Chemischen Fabriken, Unfallsverhütungsmittel und Arbeitsbedingungen Eine durch den Englischen Parlamentsbericht von 1893, veranlasste kritische Besprechung Englischer und Deutscher Industrie verhältnisse"). By KONRAD W. JURISCH, Docent at the Royal Technical High School of Berlin. Berlin: R. Gaertner. 1895.

THE report presented by the Chemical Works Committee of Enquiry of 1893 is, of course, well known in this country. Still, it is interesting to see how its conclusions and recommendations appear to a foreigner who has the advantage of personal acquaintance with the heavy chemical trades, and has resided for some time at St. Helens and Widnes. The Committee of Inquiry, unlike the late Rivers' Pollution Commission, had the advantage of including two physicians, whose special reports on the physiological actions of the conditions to which the workmen are exposed are eminently judicious.

As remedies for the effects of chlorine and of corrosive gases, the men have recourse to brandy or whisky. Dr. Jurisch found that they were ignorant of the employment of ammoniacal vapours, and could not be taught to use them. The present writer has often found personally and observed on others much benefit from sips of the strongest vinegar or dilute acetic acid. That Dr. Jurisch is closely acquainted with the effects of irrespirable gases is proved by the fact that he advises men in such cases to retire slowly, taking only slight superficial breaths of air until reaching a purer atmosphere. To take a full breath is exceedingly hazardous and might conceivably be fatal. The fact that certain precautions in vogue on the Continent are neither practised in English chemical works nor proposed by the Commissioners, Dr. Jurisch ascribes to the different conditions of work, and, above all, to the carelessness of the men and their aversion to be taught anything. He points out that the administration of ammonia to a man half suffocated with chlorine unless effected with judicious care may increase the mischief.

To a careful sober man the manufacture of chloride of lime presents far less dangers than has been represented by sensational writers. It is shown that relatively shallow layers of lime in the chloride chambers, which do not require to be turned over, are in reality preferable, as well from an industrial as from a hygienic point of view.

Small quantities of hydrochloric acid in the air do not interfere with respiration, improve the appetite, and occasion no inconvenience beyond "setting the teeth on

edge." Vapours of sulphuric acid are more pernicious. It is remarked that boys under eighteen years of age are not employed in the manufacture of chloride of lime and of sulphuric acid, and that women are altogether excluded.

Caustic soda presents its dangers; a fall into the melting-pans is almost inevitably fatal. Hence it would be well if care were taken in British works, as in those of France and Germany, to exclude any man from work in this department who is not sober.

It is here remarked that in Continental works the mixture of lime-water and linseed oil, invaluable as a remedy for burns, is kept ready for use on a large scale. In England and Scotland it has been in use to our certain knowledge since 1857, under the name "Carron oil." The Commission did not think it necessary to mention so well known a remedy.

The use of lead acetate as an application to the eyes in case of a spurt of acid or alkali dates back to the same year, and that at a works in Widnes which certainly made no speciality of care for the sanitary well-being of the workmen.

This Report, both in its original form and in the German annotated and critical version, will be of great service in leading to hygienic improvements which can be introduced without interference with the manufacture.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxi., No. 14, September 30, 1895.

The Death of Louis Pasteur.—A. Cornu, the President, delivered an eloquent discourse on the eminent merits of the discoverer whom the world, and more especially France, has just lost.

Remarks on the Discourse of Lord Salisbury on the Present Limits of our Science.—Emile Blanchard. —In the shape of a notice of the Presidential Address delivered by the Marquis of Salisbury at the Oxford Meeting of the British Association (1894), M. Blanchard has repeated the threadbare challenge of the anti-evolutionists, that if anyone will show an instance of the transformation of a species he will confess himself mistaken! He knows perfectly well that his challenge presupposes the impossibility of a naturalist living and observing for a few thousand years.

New Nitrogenous Manure: Calcium Cyanate.—Camille Faure.—The substance in question is calcium cyanate, $\text{Ca}(\text{CNO})_2$, hitherto a laboratory curiosity, but now promising to become an important substitute for nitrate of soda, and even containing a larger proportion of assimilable nitrogen. A mixture of limestone and coke is submitted to a preliminary temperature of 1500° in an electric blast furnace, and is then superheated in the same furnace to 2500° in presence of a large excess of pure nitrogen, and finally to oxidation by means of air, the oxygen of which is retained by the product, whilst the nitrogen conveys the heat due to the oxidation into the electric chamber. The operation must be conducted in a large furnace, so that the calorific yield may be sufficiently economical. The assimilation of the nitrogen of this product by vegetation does not appear to be doubtful.

Constitution of the Acids produced in the Oxidation of Inactive Campholenic Acid.—A. Béhal.—The author claims the priority of the synthetic preparation of dimethylglutaric acid as against Dr. Tiemanns.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xiii.-xiv., No. 10, 1895.

Tindorial Properties of Glucina.—M. Prudhomme. The author explained the different tinctorial properties of sesquioxides and protoxides. The former do not become saturated with alizarin in distilled water; in order to form a solid lake they require the co-operation of lime. The second dye up equally well with or without lime. Glucina as regards dyeing behaves like a protoxide.

Ammonium Manganous Phosphate, and its Use in the Volumetric Analysis of Phosphoric Acid.—MM. Lindemann and Motten.

Preparation of Monomethylamine.—A. Brochet and R. Cambier.—The authors place 2 kilos. of commercial formic aldehyd in a three-litre flask, connected to a good refrigerator by a Wurtz tube fitted with a thermometer, and 1 kilo. of ordinary crystalline sal-ammoniac. On heating gently the liquid becomes strongly acid and takes a yellow colour. At 40° there is produced a brisk ebullition, when the heat is reduced. Methylal distils over in abundance. We then raise the temperature by degrees to 95°. The receiver is changed and the distillate contains 60 to 70 per cent of methylal. The solution is concentrated until the excess of sal-ammoniac begins to precipitate, and on refrigerating this salt is deposited almost entirely. It is drained by suction; the filtrate is a solution of monomethylamine almost pure.

Two Combinations of Mercuric Sulphate with Thiophene, allowing of the Determination of this Substance in Commercial Benzenes.—G. Denigès.—The author describes in detail the determination either in an aqueous or a methylic solution.

Ammoniated Derivatives of Hexamethyltriamidotriphenylmethan, its Carbinol, and its Mixed Ethers.—A. Rosenstiehl.—This voluminous paper does not admit of a complete abstraction. We may see that experimental proof is given that the leucobases, the magentas, and the rosanilines contain amidic-groups with the same functions. All three are triamines of the same degree; in all the three classes of compounds the three groups NH_2 fulfil the same functions without a single reaction leading to the admission that one of them is retained in the mol. of any other bond than that which retains the atom of H which it replaces in the mol. of phenyl.

The Question of Acid Magentas.—Maurice Prudhomme.—A polemical paper. The author considers that the conceptions on the nature of the acid magentas may thus be summarised:—1. The colouring and coloured matter exists as a neutral salt or an acid salt of the sulphonated carbinol. 2. The addition of a mineral acid to the salts of rosaniline liberates the latter, which is coloured.

No. 11.

Researches on Manganese.—Charles Lepierre.—Already inserted.

Hydrated Metallic Chlorides. A Reply to H. Lescœur.—Paul Sabatier.—A polemical paper.

Composition of the Wines of Samos used in the Manufacture of Vermuth.—P. Cazeneuve and M. Hugounenq.—A paper of no scientific interest.

Present State of the Production and Consumption of Phosphates.—David Levat.—A statistical account of the production of natural mineral phosphate in Florida, Carolina, Algeria, and Tunis, and of the phosphatic slags obtained by the Gilchrist process.

MEETINGS FOR THE WEEK.

FRIDAY, 25th.—Physical, 5. "The Radial Cursor," by F. W. Lancaster. "The Development of Arbitrary Functions," by Prof. Perry and Mr. Hunt.

ERRATUM.—P. 185, col. 1, line 31 from bottom, for "0.47325 c.c." read "0.47325 gram."

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THE CHEMICAL NEWS.

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OBSERVATIONS BY AID OF THE TENSIO-METER.

By J. ALFRED WANKLYN and W. J. COOPER.

THE paper which one of us prepared for (but did not read at) the Ipswich Meeting of the British Association (see CHEMICAL NEWS, vol. lxxii., p. 164) mentions our Tensiometer.

We employ two modifications of the instrument, viz., one modification designed for the measurement of low tensions, and another modification designed for comparatively high tensions.

The modification designed for low tensions is original only in some seemingly trifling details, which we hope to mention more particularly on another occasion. We confine ourselves at present to the publication of some of the earliest results which we have obtained.

Eleven consecutive terms of the Russian series of hydrocarbons, to which we have given the name kerosene, as set forth in our recent papers on this subject, have been taken for investigation. Our results are as follows:—

Name of the hydrocarbon liquid.	Tension of the vapour evolved <i>in vacuo</i> at 15° C. M.m. of mercury.
Kerosene xxiii.	1'2
" xxii.	3'5
" xxi.	6'9
" xx.	8'9
" xix.	10'0
" xviii.	14'8
" xvii.	18'0
" xvi.	31'0
" xv.	48'0
" xiv.	59'0
" xiii.	82'0

The first of these hydrocarbons boils under ordinary atmospheric pressure at 176° C., and the last at 76° C.; and it will be observed that the gradual drop in the boiling point is shadowed forth by a continual increase of the tension of the liquid at ordinary temperatures.

We have also measured the tensions of valerianic acid, acetic acid, and formic acid at 15° C. as follows:—

	M.m. of mercury.
Valerianic acid	6'0
Acetic acid	9'0
Formic acid	10'0

Now, valerianic acid has about the same boiling-point as Kerosene xxiii., and acetic acid nearly the same boiling-point as Kerosene xvii., and formic acid comes between Kerosene xv. and Kerosene xvi. There is utter want of parallelism between the fatty acid and the hydrocarbon in the matter of tension at ordinary temperatures.

Tension of acid.	Corresponding tension of kerosene.
6	1'2
9	18'0
10	40'0

The drop from the boiling-point of valerianic acid to the boiling-point of formic acid is shadowed forth by the increase from 6 to 10. But among the kerosenes a like drop in boiling-point is indicated by the increase from 1'2 to 40'0.

The first term in our table of the eleven kerosenes has a tension of 1'2 m.m. at 15° C. If we gradually raise the temperature, the tension will gradually increase, attaining

to 80 m.m. at about 96° C. When any of these kerosenes attain to a tension of 80 m.m., we are able to describe the comparatively steep section of the tension-curve with approximate accuracy. Given the point in temperature at which the tension attains to 80 m.m. we can name the boiling-point under ordinary atmospheric pressure. The rule is, add on 80° in the case of Kerosene xxiii.; add on nearly 60° in the case of Kerosene xiii., and add on intermediate numbers in the instance of the intermediate kerosenes.

THE LATEST DISCIPLE OF HERMES TRISMEGISTUS.

By H. CARRINGTON BOLTON.

THE persistence with which a belief in the transmutability of metals clings to common people in these days of universal education shows that there are still individuals in whom avarice linked with superstition are stronger characteristics than honesty in thought and action. In France the publication of alchemical processes continues, scarcely a twelve-month elapsing without an addition to this literature; in that country, too, as well as in England, claimants of the secrets of Hermes occasionally appear. Often their first appearance in public takes place in a police-court to answer charges of fraud, for the law does not recognise the veridity of alchemical professions. The case of the ingenious American who endeavoured to swindle the Bond Street jeweller a few years ago, by borrowing gold sovereigns with a promise to "multiply" them, is fresh in the minds of readers of the CHEMICAL NEWS.

In September of this year an extraordinary exhibition of faith in alchemy occurred in New York City, the details of which remind us of similar transactions reported in the Middle Ages.

The persons in this domestic drama are four in number—a small tradesman, Gustav Hammer, by name, and his wife, who became the dupes of two conspirators named Stanley Glass and Max Pearlman. In the spring of 1895 Glass confided to Hammer that a friend of his possessed a wonderful secret which would make them all rich; his friend, he explained, was an alchemist, and with a little brass, some copper, and a few platinum filings, and the wonderful secret, he could procure any amount of gold. These representations interested Hammer and his wife, who consented to go into the business. Soon after, Glass introduced his friend Pearlman as the possessor of the Philosopher's Stone, and these two induced Hammer to furnish the money necessary for an experiment; the latter gave the reputed alchemist 4.50 dols. for platinum and 234 dols. for other materials. After some delays and procrastination on the part of Pearlman, the great work was undertaken in his house.

The experiment was conducted in a semi-dark room, and began at midnight. The metals were placed in a crucible over a very hot fire, and Pearlman stirred them with a rod, at the same time pouring in a white powder—the Philosopher's Stone. The heat was maintained for a long time until the metals fused. After cooling the crucible, Pearlman took out the alloy and gave it to Hammer, saying it was pure gold. The tradesman took the fused mass to an assayer, who informed him the lump contained 18 dols. worth of gold.

So far this resembles a page from the career of Sendivogius, but the sequel is very different. Hammer, indignant at the swindle, sought relief in the courts, and on his representations the Grand Jury indicted Stanley Glass and Max Pearlman. During the taking of testimony, it appeared that Mary Pearlman, the alchemist's wife, had sought to have the case dropped by offering various sums of money—beginning with 60 dols. and rising to 100 dols. This was corroborated by Mrs. Louisa Hammer.

At the last accounts, Glass had been arrested, but Peariman could not be found. Verily, the good old times of Cagliostro have departed!

QUANTITATIVE ANALYSIS BY MEANS OF ELECTROLYSIS.*

A PRELIMINARY report was furnished by the Committee last year in which the contemplated plan of work was outlined.

The bibliography of the subject has been completed and is appended.

The experimental work has been carefully organised, and the results on the determination of bismuth and of tin are nearly complete. Other work is in progress, but the Committee prefer to hold over these results until next year in order that they may be added to and may include methods of separation of some of the metals.

Considerable attention has been given to the choice and arrangement of the special apparatus required. A detailed description of some of the arrangements adopted will be given in the next report.

As the bibliography is completed, the Committee propose to devote their attention during the coming year exclusively to experimental enquiries.

Bibliography on Methods of Quantitative Analysis by means of Electrolysis.

The bibliography has been compiled from the following journals, and is complete up to the end of 1894:—

Journal.	Period abstracted.	Abbreviation.
1. Journal of the Chemical Society	1847-1894	J. Chem. Soc.
2. Journal of the Society of Chemical Industry	1882-1894	J. Soc. Chem. Ind.
3. Chemical News	1860-1894	Chem. News.
4. American Chemical Journal	1878-1894	Amer. Chem. J.
5. Journal of Analytical and Applied Chemistry.. .. .	1887-1894	J. Analyt. and App. Chem.
6. Journal of the American Chemical Society	1879-1894	J. Amer. Chem. Soc.
7. Zeitschrift für Analytische Chemie	1862-1894	Zeits. anal. Chem.
8. Berichte der Deutschen chemischen Gesellschaft.. .. .	1868-1894	Ber.
9. Zeitschrift für anorganische Chemie	1892-1894	Zeits. anorg. Chem.
10. Zeitschrift für physikalische Chemie	1887-1894	Zeits. phys. Chem.
11. Zeitschrift für Electrochemie. (Organ der deutschen electrochemischen Gesellschaft)	1894	Zeits. Electrochem.

References to papers of importance published in journals other than the above are also included.

Books of Reference.

1. "Quantitative Analyse durch Electrolyse." A. Clausen. 3rd edit., 1892. Published by J. Springer, Berlin.

* Read before the British Association (Section B), Ipswich Meeting, 1895. (Second Report of the Committee, consisting of Prof. J. Emerson Reynolds, Chairman, Dr. C. A. Kohn, Secretary, Prof. P. Frankland, Prof. F. Clowes, Dr. Hugh Marshall, Messrs. A. E. Fletcher, D. H. Nagel, T. Turner, and J. B. Coleman).

Translation, by W. H. Herrick, of 2nd edition, 1887, "Quantitative Chemical Analysis by Electrolysis." Published by I. Wiley, New York.

2. "Electro-chemical Analysis." Edgar F. Smith. 1890. Published by P. Blakiston, Philadelphia.

3. "Jahrbuch der Electrochemie." W. Nernst and W. Borchers. 1894 (first year of publication).

Arrangement of Bibliography.

The bibliography is divided into the following sections:—

1. General conditions for electrolytic analysis.
2. Special apparatus employed.
3. Quantitative methods, for the determination of metals by means of electrolysis.
4. Quantitative methods, for the separation of metals by means of electrolysis.
5. Special applications of electrolysis in quantitative analysis.
6. Applications of electrolysis to qualitative analysis.

THE PERIOD - TABLE.*

By F. RANG.

THE space in the Table between C, Si, and A, IV, b , is not a real one, but only an unavoidable defect similar to that encountered when a globe is mapped on a plane surface.

Every sign in this Table signifies not only its usual element, but also every other element in the same series, valency, and part of the Table. La and Yb signifies, therefore, La, Ce, Ny, Py, Sm, Tb, Ho, Er, Tm, Yb, and perhaps as many more yet unknown elements. Their atom-volumes and chemical activity show that they do not make a series.

Several facts indicate that H is here put in its right place. Now when A is found we no longer have any right to be incredible about the existence of the elements marked (+), and, moreover, we are able in some places of the Table to predict where they are to be found, e.g., which elements the explorer could use as ores. We are also able in some degree to predict their general properties.

What is now known about A, together with its periodic arrangement, tells us that it has the molecule—



atomic weight 13, and valence IV. A glance at the molecular formula of A will explain its resistance to chemical action; its molecule is not easily broken, but when its atoms are once separated, it is likely to get an extended chemistry.

Table of Half-forgotten Elements.

	Atomic weights.		Reference.
	Probable.	Derivation.	
Davium, Da, sp. gr. 9.39	100	$\frac{1}{2}$ (150—154)	xxxvii., 65
Uralium, (Url), sp. gr. 20.25	187	187	lviii., 188
Norwegium, Ng, sp. gr. 9.44, m.p. 350° C.	64	$\frac{1}{2}$ (145)	
Austriacum, (Ast)	212	212	lix., 295
Neptunium, Np	236	2 (118)	xxxv., 197
Ilmenium, Il	?	104.6	xxxv., 197
Polymnestum, Pm.. .. .	?	74	
Erebodium, Eb	94.5	94.5	Of the group Ti—W.
Gadenium	?	43.5	
X, X' X''	?	?	

* See CHEM. NEWS, vol. lxxvii., p. 178.

Valence. I.	II.	III.	IV.	V.	VI.	VII.	VIII.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Series.															
1.	Li	Be	B	C	..	..	..	..	..	H	He	+	(+)	(?)	
2.	Na	Mg	Al	Si	..	..	..	..	..	..	A	N	O	F	(?)
3.	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Ni	Co	..	(+)	P	S	Cl
4.	Rb	Sr	Y	Zr	Nb	Mo	Da	Ru	Rh	Pd	Cu	Zn	Ga	Ge	As
5.	Cs	Ba	La	Yb	Ta	W	Url	Os	Ir	Pt	Ag	Cd	In	Sn	Sb
6.	(+)	Ms	(+)	Th	Np	U	(?)	(?)	(?)	(?)	Au	Hg	Tl	Pb	Bi
7.															Ast

4III.a = Sc, Pp. 4I.b = Cu, Ng. 6III.a and 6IV.a = La, Ce, Ny, Py, Sm, Gd, Tb, Ho, Er, Tm, Dc, Yb. . .

* Unnamed element accompanying helium.

A most of all known substances violates Dulong and Petit's law, and also the general application of Avogadro's law; it has next to H the highest specific heat of all elements; its light-refraction is low in proportion to its specific gravity, but its atomic volume corresponds exactly to its place in the diagram of the atom-volume-series. (The atomic volumes for C, A, and N are 3.4, 8.7, and 15.3).

As some of the elements in my Table have not been introduced before in any period-table, and are therefore unknown to many, I have, for what good it might be, put together the Table in preceding column.

The sp. gr. of Da and Url give a peculiar and verifying shape to the corresponding parts of the diagram over the atom-volume-series. Probably He and its side-elements give similar diagram verifications.

I claim that my period-table is the truest and best tabular arrangement of the elements yet produced; that the table has place for all elements, and fulfils every proper requirement of to-day.

EXPERIMENTS ON THE VAPOUR-PRESSURE OF CONCENTRATED SOLUTIONS OF SEVERAL SALTS, ESPECIALLY LITHIUM AND CALCIUM NITRATES.

By JOHN WADDELL, B.Sc. (Lond.), Ph.D. (Heidelberg),
Professor of Chemistry, Royal Military College of Canada.

THE experiments, of which those described here are a few, were undertaken at the suggestion of Dr. Goodwin, who had himself sent some reports to the British Association, recording the relative amounts of water-vapour absorbed by sodium and potassium chlorides, when exposed to the same atmosphere. They were begun before the late development of the theory of solutions and the law of vapour-pressure had been enunciated, and a good deal of the work done is not now of much value, and I therefore do not go into the detail that I should otherwise have considered advisable. The majority of experiments on vapour-pressure have, however, been made with very dilute solutions; in these which I describe solutions much nearer the saturation-point were employed.

The method adopted was that to which the name Inavaporation was applied, I believe, by Graham, and was carried out in the following manner:—

Into a wide-mouthed closely-stoppered bottle, of about 200 to 300 c.c. capacity, three small test-tubes were introduced, one of which contained water or alcohol, and each of the others one of the salts to be experimented with. After some experience had been gained, the liquid was frequently added directly to the salts, and the third test-tube dispensed with.

The salts first chosen for experiment were calcium and lithium nitrates; nitrates being selected because Dr. Goodwin had worked with two chlorides, and these particular nitrates being chosen because both soluble in alcohol as well as water.

The quantities of salts taken were molecular, weighed in m.grms.; but 1, 2, or 4 mols. of one salt was taken to

1 mol. of the other, so that in some experiments there was a larger amount of calcium nitrate, in others of lithium nitrate. So far as the results recorded here are concerned there was no necessity for this variation, because the numbers retained are all reduced so as to show the quantity of liquid inavaporated *per molecule* of the salts. When there was a great excess of one salt, however, and a small amount only of the liquid, it sometimes happened that the latter was entirely absorbed by the salt which was in relatively large quantity; for example, when there were 8 mols. of calcium nitrate to either 2 or 4 mols. of lithium nitrate, and only about a decigram of water, the latter was all absorbed by the calcium salt, and the result was nearly the same when alcohol was the liquid.

Table of Quantities of Water taken up by 0.164 grm. of Calcium Nitrate and 0.069 grm. of Lithium Nitrate.

1 Ca(NO ₃) ₂	0.189	0.299	0.367
1 LiNO ₃ ..	0.142	0.232	0.299

These numbers obtained from experiments in which there were 4 mols. of calcium salt to 1 mol. of the lithium.

1 Ca(NO ₃) ₂	0.125	0.144	0.161	0.241	0.317
1 Li(NO ₃) ..	0.089	0.108	0.124	0.194	0.265

From experiments in which the ratio of calcium to lithium was 2 : 1.

1 Ca(NO ₃) ₂	0.150	0.221	0.218	0.295	0.423
1 LiNO ₃ ..	0.105	0.167	0.171	0.230	0.339

From experiments in which the ratio of calcium to lithium was 1 : 4.

1 Ca(NO ₃) ₂	0.137	0.180	0.217	0.264	0.459	0.521
1 Li(NO ₃)	0.100	0.135	0.172	0.202	0.327	0.403

From experiments in which the ratio of calcium to lithium was 1 : 2.

1 Ca(NO ₃) ₂	0.123	0.129	0.188	0.246	0.248
1 Li(NO ₃) ..	0.044	0.093	0.145	0.196	0.198

1 Ca(NO ₃) ₂	0.365	0.476	0.952	4.228
1 LiNO ₃ ..	0.298	0.410	0.819	3.619

From experiments in which the ratio of calcium to lithium was 1 : 1.

If a curve is plotted whose ordinates are the quantities of water absorbed respectively by the lithium nitrate and the calcium nitrate, it does not differ very much from a straight line, though it is slightly concave towards the axis of the lithium nitrate.

The three cases given in which the amount of water absorbed by the molecular weight of lithium nitrate was less than 0.1 grm. represent what was found to be the general phenomenon, namely, that the calcium nitrate absorbed between 0.120 grm. and 0.130 grm. of water, and had a vapour-pressure equal to that of the saturated solution of lithium nitrate. Hence, while the amount of water absorbed by the calcium nitrate remained practically constant, the quantity absorbed by the lithium nitrate was different in the different experiments, there being more or less of the salt undissolved. After this limit had been passed, the ratio of the water absorbed by the lithium nitrate to that absorbed by the calcium nitrate ranged from about four-fifths to five-sixths.

The formula of lithium nitrate being LiNO_3 , and of calcium nitrate $\text{Ca}(\text{NO}_3)_2$, if all the molecules of each were dissociated into their ions there should be the same vapour pressure when the amount of water absorbed per molecule is in the ratio of 2 : 3.

It is therefore plain that the lithium nitrate is dissociated to a greater extent than the calcium nitrate. The ratio of 5 : 6 would be obtained if two-thirds of the lithium nitrate were dissociated and one-half of the calcium nitrate.

In an experiment made with potassium nitrate and calcium nitrate, it was found that 1.932 grms. of water was absorbed by a molecular weight of the former, and 2.836 grms. of water by a molecular weight of the latter.

Suppose half of the calcium nitrate to be dissociated, it would follow that one-third of the potassium nitrate is dissociated. If it is known to what extent any one of the three is dissociated, then it would be known to what extent the others are dissociated, but otherwise the ratios give rise to indeterminate equations only.

Experiments were also made with alcohol as the liquid evaporated. There was less uniformity than in the case when water was employed, partly because the alcohol doubtless contained water, as it had not been dried with sodium, but was what had either been bought as absolute or what had been twice distilled over lime. The result may have been partly produced, also, by the fact that it was difficult to make the bottles tight enough to prevent the escape of a little alcohol-vapour. Burnt rubber digested in alcohol was found to be the most satisfactory of the different substances tried for the purpose of keeping the stopper tight.

The numbers given were calculated in the same way as in the preceding case with water. It will be seen that not only does the lithium nitrate absorb more alcohol than it should if the calcium nitrate were equally dissociated, but molecule for molecule an amount absolutely greater. Each molecule of lithium nitrate absorbs approximately four-thirds as much alcohol as each molecule of calcium nitrate. This condition would be fulfilled if all the lithium nitrate were dissociated, and one quarter only of the calcium nitrate molecules.

Table of Quantities of Alcohol taken up by 0.164 grm. of Calcium Nitrate and 0.069 grm. of Lithium Nitrate.

1 $\text{Ca}(\text{NO}_3)_2$	0.194	0.312	0.408	0.612
1 LiNO_3	0.324	0.427	0.575	0.889

From experiments in which the ratio of calcium to lithium was 4 : 1.

1 $\text{Ca}(\text{NO}_3)_2$	0.178	0.256	0.341	0.474	0.618	0.935
1 LiNO_3	0.220	0.332	0.460	0.696	0.896	1.388

From experiments in which the ratio of calcium to lithium was 2 : 1.

1 $\text{Ca}(\text{NO}_3)_2$	0.224	0.266	0.372	0.600	1.236
1 LiNO_3	0.280	0.331	0.469	0.845	1.552

From experiments in which the ratio of calcium to lithium was 1 : 2.

1 $\text{Ca}(\text{NO}_3)_2$	0.204	0.283	0.360	0.533
1 LiNO_3	0.244	0.368	0.480	0.726

From experiments in which the ratio of calcium to lithium was 1 : 4.

1 $\text{Ca}(\text{NO}_3)_2$	0.482	0.718
1 LiNO_3	0.657	0.987

From experiments in which the ratio of calcium to lithium was 1 : 1.

In order to compare the members of the calcium group of metals among themselves and with lithium nitrate, a series of experiments was instituted. Barium and strontium nitrates being less soluble than calcium nitrate, a larger quantity of water was needed than for the calcium and lithium salts, and within the limits in which I have hitherto worked the results are not very concordant; but I give the numbers without delaying the paper for the further investigations which I propose making, and which

will take some time. There seems to be little doubt, from what has been done, that the barium nitrate is the most absorbent; that the calcium salt comes next; and that the strontium compound, instead of being intermediate between the others, is less absorbent than either.

Table of Quantities of Water absorbed by each Molecular Weight expressed in Milligrammes.

1 LiNO_3	—	—	0.460	1.182	—
1 $\text{Ca}(\text{NO}_3)_2$	0.590	1.166	—	—	0.797
1 $\text{Sr}(\text{NO}_3)_2$	0.504	1.115	0.470	1.320	0.685
1 $\text{Ba}(\text{NO}_3)_2$	—	—	—	—	—
1 LiNO_3	0.327	0.761	—	1.339	—
1 $\text{Ca}(\text{NO}_3)_2$	—	—	8.205	[1.607]	—
1 $\text{Sr}(\text{NO}_3)_2$	0.331	0.830	—	[1.495]	—
1 $\text{Ba}(\text{NO}_3)_2$	—	—	8.994	1.671	—

The relationship spoken of above will be seen in the last column. The unbracketed numbers are the result of direct experiment; of the bracketed numbers that for calcium nitrate is obtained by calculating the water absorbed by that salt as six-fifths the amount absorbed by lithium nitrate, and that for strontium nitrate is deduced from the figures in the fourth column, where it will be seen that strontium nitrate absorbs 1.320 grms. of water for 1.182 grms. absorbed by lithium nitrate.

Finally, a series of experiments was made in which the metal was the same, but the salt radical varied. The haloid salts of potassium were chosen for experiment. It appears that these salts are very nearly equally dissociated, even in rather concentrated solutions, but if anything the bromide is more dissociated than the others.

Table of Quantities of Water taken up by the Milligramme Molecular Weight of Potassium Chloride, Bromide, and Iodide.

1 KCl	0.060	353	553	126	506	797
1 KBr	0.229	377	588	—	—	—
1 KI	0.229	373	581	229	522	797
1 KCl*	2.070	0.088	0.312	747	2.237	—
1 KBr	—	0.229	0.326	784	2.339	—
1 KI*	1.933	0.229	0.328	802	2.310	—
1 KCl	0.595	295	248	411	605	1.190
1 KBr	0.606	311	251	—	—	—
1 KI	—	—	—	428	624	1.205
1 KCl	200	407	1.027	266	690	376
1 KBr	—	—	—	296	—	396
1 KI	226	431	1.057	—	—	—
1 KCl	781	401	781	769	188	560
1 KBr	827	—	—	—	—	238
1 KI	—	415	789	775	233	589

(NOTE.—The numbers marked with the asterisk are peculiar, as in no other case does the KCl absorb more water than the KI. In this instance more water had been added originally to the chloride than to the iodide, and in evaporation does not seem to have been complete even after a lapse of two years. It turned out that some water-vapour escaped from the bottle, for a weighing made since this paper was written, and six months after the one recorded above, gave KCl 2.033 and KI 1.931. Thus the main loss was from the chloride, and I have no doubt that now that the stopper has been made tight the anomaly will disappear.

When the quantity of water to be divided among the salts was small, a phenomenon, similar to that observed with the lithium and calcium nitrate, is again prominent. The bromide and iodide absorbed the water, the chloride apparently being left dry until the other salts had absorbed a considerable quantity of water.

In two cases the bromide and iodide have 229 m.grms. of water each, while the amount of water with the chloride is in one case 60 m.grms. and in another 88

m.grms. In another experiment the same number 229 is found for the iodide, while the chloride has 126. Still another experiment gives 226 with the iodide and 200 with the chloride. We may therefore conclude that the bromide and iodide would probably absorb a constant amount of water whenever the quantity is more than 450 m.grms. and less than a little over 650 m.grms., and that the chloride absorbs what is left over.

So soon as this limit is passed, the three salts absorb nearly the same amounts of water, as shown by the case in which the bromide absorbed 257 m.grms. and the chloride 248 m.grms. It appears, then, that the bromide and iodide of potassium both absorb enough water to make a solution, while the chloride is still in the solid condition, and when the vapour-pressure from the bromide and iodide comes to be as large as that of the saturated solution of the chloride it remains constant until the chloride is all dissolved.

The peculiarity of the lithium nitrate, as compared with calcium nitrate, is the most noticeable feature in the experiments, and I have therefore begun some experiments with chlorides and sulphates, which, however, will require time for completion. Meantime I made a rough set of experiments, on the electrical resistance of strong and dilute solutions of lithium and calcium nitrates.

6.9 grms. of lithium nitrate were dissolved in 100 grms. of water, and to 10.277 grms. of this solution 349 grms. of water were added.

In the same way, a strong and a dilute solution of calcium nitrate was made. 8.2 grms. of calcium nitrate were dissolved in 100 grms. of water, and to 10.377 grms. of this solution 352.4 grms. of water were added.

The resistance of these liquids was determined in the following manner:—

The vessel containing the solution was put in circuit, with Lord Kelvin's composite balance and his set of anti-inductive resistance-coils. An alternating current, such as used for incandescent lighting purposes, was employed, and its electromotive force was determined by a statical voltmeter. The current was read directly from the balance, the difference of potential was given by the voltmeter, and therefore the resistance could be calculated. Since the resistance in the box was known, the resistance of the solution could be calculated by subtracting it from the total resistance. The vessel in which the liquid was contained, whose resistance was measured, was a U-tube of about 30 c.c. capacity. The electrodes were kept at the same distance, in the different experiments, by resting on the ledges produced by the narrowing of the tube at the bend.

The average resistance of the strong solution of calcium nitrate was 238 ohms. The average resistance of the dilute solution was 3690 ohms. In the case of the lithium nitrate the resistance of the strong solution was 167 ohms, and of the dilute solution 4114 ohms. If the salts had been equally dissociated in the strong and dilute solutions, and if the current is carried only by the dissociated ions, the resistance of the dilute solutions of the calcium nitrate should have been 8100 ohms, and of the lithium nitrate 5827 ohms. The resistance of the calcium nitrate actually increases in a much less ratio than the dilution, while the lithium nitrate does not show so great a divergence.

The amount of dissociation of the calcium nitrate is about 45 per cent as great in the strong solution as in the weak, while the amount of dissociation in the case of the lithium salt is about 83 per cent.

Owing to several sources of error, such as the fluctuation of the electromotive force of the circuit, and the difficulty of taking accurate readings, when the current was small, the results attained do not pretend to close exactness; but they show the nature of the change produced by dilution, and that in the strong solution calcium nitrate is much less dissociated than lithium nitrate. Moreover, the result obtained for the latter salt does not differ very greatly from that given for lithium chloride in

Ostwald's "Outlines of General Chemistry" (English edition, p. 261).

Nearly all of the experiments in invaporation recorded above were with solutions more concentrated than even the nearly normal solutions, which were the strongest employed for the determination of electrical resistance.

It was stated that the ratio obtained between the quantities of water absorbed by the two salts, when the vapour-pressure was the same, would be satisfied if two-thirds of the lithium nitrate were dissociated and one-half of the calcium nitrate.

The table given by Ostwald shows that in the normal solution of lithium chloride the dissociation is about 61 per cent, and my experiments on the electrical resistance seem to show that lithium nitrate is somewhat similar to the chloride. Very probably, then, this calculation is not very far astray.

I should perhaps add that the bottles containing the tubes with which the invaporation experiments were made were at the temperature of the laboratory, which varied between 10° C. and 25° C. at different times of the year. I have weighed the same tube, however, in spring and autumn, and the weight was within a m.grm or two the same, so that the variations of temperature had no appreciable effect.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 190).

So long as a spectroscopic examination enables one to detect the presence of sodium in a flame burning in air, either *at rest* or *in motion*, this air imparts to platinum, in whatever state it may be, the property of colouring the flame yellow. Spongy platinum possesses this property in a marked degree.

The time necessary for the deposit of sodium on platinum is very variable; with the ordinary air of the laboratory from ten to fifteen minutes are sufficient, whilst several days' exposure are necessary for producing the yellow colour in the flame when the air only shows slight traces of sodium.

Even spongy platinum, when kept lying in a glazed cupboard in dry air, in which spectrum analysis is unable to detect the presence of sodium, only acquires the property of turning a flame yellow after several days' exposure; but a spectrum analysis of the flame *before it has changed colour* shows a faint image of the sodium D line.

It follows from these experiments that it is always the air which deposits sodium on platinum.

Silver behaves like platinum. When properly refined, as I have described, it shows no trace of the sodium spectrum. After having been left in air in which spectrum analysis shows a bright yellow sodium line, it imparts a distinctly yellow tint to a Bunsen burner flame, and shows a strong sodium line. This colour quickly disappears; but if the metal be covered with atmospheric dust it colours the flame yellow, and this property remains until it has been melted and properly refined in a lime crucible.

The tubes and silver fittings, when kept in air, should be carefully washed with water mixed first with hydrofluoric acid, then with hydrochloric acid, and afterwards with pure water.

Bone-black when refined behaves exactly like platinum and silver. It attracts the deposit of sodium. It should be kept in *air-tight jars*, and should never be used until after having been raised to white heat.

Platinum, silver, and carbon, when kept *protected from atmospheric dust* in cupboards, well-closed glass cases, under bell-jars, &c., acquire a deposit of sodium on their

surfaces. The sodium is evidently contained in the outside air which continuously mixes by *diffusion* with the air inside the cupboards, cases, and jars. The rapid deliquescence of highly soluble compounds, when left in these confined spaces, is evidence of the rapid rate of diffusion. This fact, moreover, is known to everybody who puts drying agents into cases, however air-tight they may be, to preserve instruments or chemical compounds from the action of water vapour in air.

Experience has taught me that one must moisten the inner surface of the tubes and metal or rubber fittings used to bring the gas from the reservoir to the apparatus, and never to use rubber tubes desulphuretted by placing them in a boiling solution of dilute hydro-oxide of sodium. When undertaking this desulphuretted one day I lost time in looking for the reason of the presence of a great deal of sodium. The soda penetrates into the rubber; the illuminating gas, by attacking it, charges itself with sodium when passing through a rubber tube desulphuretted with hydrate of sodium, even although the tube has been washed with water containing a little acid and then dried.

It was by pondering over the above facts and conclusions that I sought to solve the problem of ascertaining if it be possible to obtain metals and metallic compounds, which, at the highest temperature attainable, should not show the characteristic spectrum of sodium on spectroscopic examination, and whether one could thus change the spectrum of metals the one to another, or at least produce the characteristic rays of the spectrum of one metal by using a compound of another metal.

Having described my researches on the spectra of the metals on which the experiments were conducted, I must describe the method used to vapourise them and the instruments I used.

On the Methods of Volatilising Metals and their Compounds.

I have used, one after the other, all known methods for attaining this end: they consist of the introduction of the bodies into—

1. The outer envelope of the Bunsen burner flame.
2. The outer envelope of a pure hydrogen flame issuing from a platinum blowpipe.
3. A blowpipe jet of pure hydrogen and pure air.
4. A jet of pure hydrogen raised to incandescence by the admixture of oxygen.
5. A jet of coal-gas rendered colourless by the admixture of oxygen.
6. The internal cone of an oxyhydrogen blowpipe.
7. The internal cone of an oxy-coal-gas blowpipe.
8. An induction-spark from 2 to 5 m.m. between the points, with or without condensers capable of giving respectively sparks of 5, 15, and 45 c.m. length, the substance being either solid, or melted, or in solution in pure or acidulated water, and either in air or hydrogen.
9. A discharge from 5 to 10 m.m. between the points, capable of giving sparks from 15 to 45 c.m. long, having from one to five very large Leyden jars intercalated, the substance being either solid or dissolved in acidulated water, and either in air or hydrogen.
10. An electric arc formed successively between pure carbon electrodes: 1st, by 30, 50, 100, or 200, of the very largest Bunsen cells; 2nd, by a battery of 33 Julien accumulators, giving at the terminals of the lamp 10 amperes and 30 volts, and forming an arc 9 m.m. long by about 8 m.m. diameter; 3rd, by a Gramme and Siemens dynamo coupled, giving at the terminals of the lamp from 28 to 30 amperes and from 60 to 80 volts, and forming an arc 2½ c.m. long by about 8 m.m. diameter; 4th, by a 10,000 candle power dynamo.*

* In the descriptions of the luminous spectra of sodium, lithium, calcium, strontium, barium, and thallium, I give details of the use made of the arcs from different batteries and dynamos.

These methods having been previously used, and their applications being known, I can limit my description to pointing out some facts that long practice has taught me.

On the Position to be given to Flames when Examining their Spectra.

Messrs. Bunsen and Kirchhoff recommend placing the dark part of an ordinary gas flame or a hydrogen flame in front of the slit in the collimator, and putting the platinum wire loop, or coil, with the compound to be vapourised, in the middle of the outer envelope of the flames on the side opposite the slit.

It is a well-known fact that, with a minute quantity of incandescent vapour, we can produce spectra which leave nothing to be desired on the score of distinctness, when the light thus obtained is sufficiently intense; but this condition can only be realised when working with very volatile bodies. It is not the same with less volatile compounds. In this case it seems better to set the jets beside the collimator so that the *right* or *left* edge of the flames is exactly opposite the slit with the centre of the edge in the axis of the collimator. By arranging it thus, one gets all the rays proceeding from a compound vapourised in the middle of the outer envelope of the flames. To satisfy oneself that this arrangement intensifies the light, it is sufficient to compare the spectrum of chloride of barium in both positions in the same flame, whether Bunsen burner or hydrogen. I am aware that under these conditions the rays have not all the same focus; but the same inconvenience is found in the usual method, because, when introducing the substance to be volatilised, one almost always pierces through the dark envelope and penetrates too far into the flame. I am willing to admit that the method I have adopted is less convenient than the one generally used, and that it requires practice to do it quickly. The difficulty of doing it is a good guarantee for the accuracy of the result. It is, in fact, necessary to place the flame so that the centre of its dark envelope is exactly on the axis of the collimator; this necessitates the absolute immobility of the flame—an immobility hard to obtain in a room where the air is more or less in motion, but still it may be obtained by using screens to shield the flame from air-currents, or, better still, by maintaining a constant pressure of from 2 to 4 c.m. of water by means of a hydrogen and air or coal-gas and air blowpipe, with a burner ending in a platinum nozzle with a hole from ¼ to 1 m.m. in diameter. With the flame in this position, using a sufficiently narrow slit, one avoids, as far as possible, oblique rays, and the background of the spectrum is always dark, whether there be lines or no. By the usual method a continuous spectrum appears so often that all spectroscopists imagine potassium and sodium to have a continuous spectrum, although I have proved that the parts in the neighbourhood of the sodium D line or potassium lines are completely free from luminosity, even although the potassium and sodium compounds be put into almost incandescent hydrogen, such as an oxyhydrogen blowpipe fed with a proper quantity of oxygen. The easiest method of adjusting the flames is as follows:—On one side I arrange on a board, on the table of a strong camera-stand used to carry the spectroscope, the Bunsen burner, and the hydrogen, hydrogen and air, oxyhydrogen, or oxy-coal-gas blowpipe, surrounded by screens to protect them against lateral air-currents. This board, the length of which is nearly half the width of the table, moves by means of an endless screw at right angles to the axis of the collimator of the spectroscope. To effect this the worm works in an easily turned screw, which is fixed by its collar in a bearing on the *left* side of the table.

On the other side, on a second board, which occupies the right half of the table, I arrange the holder used in putting the compounds into the outer envelope of the flames. The second board also moves at right angles to the axis of the collimator, by means of an endless screw attachment on the *right* side of the table.

By this means the endless screw attached to the board on the left causes the burner or blowpipe on it to advance or recede from left to right, whilst that on the right causes the holder on the other board to move forward or back from right to left.

As the pitch of the screw is very fine, a millimetre at the outside, one can bring the rays from the incandescence vapour under spectroscopic examination into the axis of the collimator of the spectroscope with great accuracy.

This arrangement enables the observer to move either the flame or the holder without removing his eye from the eyepiece of the spectroscope; this is necessary when he only has small quantities of matter to deal with, because he can work alone without injuring the relative purity of the air, and at the same time avoid any error following the appearance of a line caused by disturbing the flame.

Experience has taught me that in order to completely avoid a continuous spectrum, one must eliminate rays from the incandescent holder. These rays extend farther than is generally thought. In many cases they extend more than 2 c.m. along the holder. One effect is this by putting the compound into the flame at least two centimetres from the edge of the slit through which the rays pass, and by arranging in front of the slit in the collimator movable platinum diaphragms which can be opened or closed at will, according to the height of the luminous beam required to pass the slit. Many spectroscopes actually have an attachment for this purpose, especially the large instruments made by M. Hilger.

I have already described the Bunsen burner as much as is necessary, so I need say nothing further about it.

On the Blowpipe.—As for the apparatus used for producing the hydrogen jet, or the hydrogen and air, oxy-hydrogen, coal-gas and air, or oxy-coal-gas blowpipe, it consists of a tube of platinum, silver, or copper, according to circumstances, bent near its free end to a right angle, ending in a nozzle of platinum, silver, or pure gold. The bore of the nozzle is from $\frac{1}{4}$ to 1 m.m. diameter, according to the length of flame I want to obtain with a constant pressure of 2 or 4 c.m. of water, measured by a manometer inserted between the blowpipe and the gasometers. I use a platinum nozzle, with an opening $\frac{1}{8}$ m.m. wide and 1 c.m. long, when I want a simple sheet of burning hydrogen. Before being adjusted to the bent tube, the nozzles are always washed with dilute hydrofluoric and hydrochloric acids, then with pure water, and finally heated to redness.

To guard against explosions, I use as a blowpipe the well-known apparatus employed by Mr. G. Matthey for fusing platinum. The mixture of gases used in it may be varied at will, by the taps fitted to it.

I think I ought to mention that it is necessary to wash and keep moistened with pure water the inside of the blowpipe, so as to prevent the presence of, and consequently avoid detaching, adherent sodium dust. The terminal tube of the blowpipe is held in a vice working on a rack on a vertical stand. The arrangements are such that I can have at will, at a pre-arranged height, a vertical, horizontal, or sloping jet, according to the conditions I have to satisfy.

In the note on the thallium line in the flame and electric spectrum, I fully explain the use of the hydrogen and air and coal-gas and air blowpipe flame.

(To be continued).

A New Black Ink.—Mr. G. Vickers, of Angel Court, Strand, is introducing a new blue-black non-corrosive ink having properties that should recommend it to the writing public. It is very fluid and dries a fine black, works well with ordinary steel pens, and does not go sticky; it will therefore be useful for stylographic pens, &c. Acids appear to have less effect upon it than upon many of the aniline inks now on the market.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING SEPTEMBER 30TH, 1895.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, October 10th, 1895.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Sept. 1st to Sept. 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 175 samples examined all were found to be clear, bright, and well filtered.

The weather during September has been in every respect remarkable, the rainfall in the Thames valley having dropped from 2.66 inches (the average of 25 years), to 0.57 inch, leaving a deficiency of 2.09 inches. Rain fell on six days only, the bulk of it, 0.39 inch, on Sept. 6th.

This, together with the excess of sunlight, has had a marked effect on the quality of the water, as can be seen by the following table:—

Comparison of the Averages of the Five Thames-derived Supplies for the Months of August and September, 1895.

	Common Salt. Per gall.	Nitric Acid. Per gall.	Hardness. Degrees. Means.	Oxygen. reqd. Per gall.	Organic Carbon. Per gall.	Organic Carbon. Per gall.	Colour. Br'n: Blue Means.
Aug. 1894	0.740	13.09	0.039	0.093	0.108	11.7	20
Sep. 1895	0.685	12.97	0.032	0.081	0.098	10.4	20

Bacteriological examinations of the filtered and unfiltered samples have been carried on unremittedly throughout the month, and we find that the average of raw unfiltered Thames water contained 2432 microbes per cubic centimetre, and river Lea water 1710 microbes per cubic centimetre; whereas the filtered samples from the five Thames Companies contained only 62 microbes per cubic centimetre, and the filtered Lea water 73 microbes per cubic centimetre.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

Researches on the Essence of Bergamot and on its Sophistications.—Dr. Ignazio Campolo. — This essence is an oily mobile liquid of a dark yellow colour, an acrid and pungent taste, and a peculiar, delightful, and penetrating odour. It has a slightly acid reaction, and a specific gravity at 15° of 0.887. Like the other essences of the Aurantiaceæ it is optically active, deflecting the plane of polarised light to the right. The principal sophistications to which essence of bergamot is liable are fatty oils and resin. The weight of residue left by the genuine essence on evaporation does not exceed 6 per cent. The increase of the weight in sophisticated samples is equal to the quantity of olive oil added.

DETERMINATION OF URANIUM IN ORES CONTAINING PHOSPHORIC AND ARSENIC ACIDS.

By R. FRESSENIUS and E. HINTZ.

IN the determination of uranium in ores containing phosphoric and arsenic acids, copper, and iron, by means of ordinary methods various difficulties were encountered. In the first place, the precipitate consisted chiefly of arsenic and copper sulphides, and sulphur could only be obtained free from uranium after repeated precipitations by hydrogen sulphide in an acid solution. Secondly, the presence of phosphoric acid greatly increases the difficulty of separating iron from uranium.

A method was therefore sought for of precipitating uranium from an acid solution, in order thus to effect the separation of phosphoric and arsenic acid. For this purpose precipitation with potassium ferrocyanide seemed a suitable means. But if the precipitation of the uranium is effected in the ordinary manner, the result is that the precipitate of uranium ferrocyanide scarcely subsides and cannot be filtered off. But if, after the addition of the potassium ferrocyanide, the liquid is saturated with sodium chloride, the precipitate quickly subsides, and can be easily filtered and washed with water containing sodium chloride.

On the basis of these facts, the determination of uranium in ores containing the above-mentioned ingredients can be executed as follows without difficulty:—

We first separate as usual the silica from the solution in nitric or hydrochloric acid or aqua regia, add an excess of potassium ferrocyanide to the slightly hydrochloric solution, and saturate the liquid with sodium chloride. The precipitate, which subsides quickly, and contains uranium-, copper-, and iron-ferrocyanides, is first washed by decantation, and afterwards on the filter completely with water containing sodium chloride, and is then treated in the cold with dilute potassa-lye. After the transformation of the ferrocyanides is completed and the hydroxides have deposited, the liquid is poured off through a filter, washed once more by decantation with water, rinsed on to a filter with a little water containing ammonium chloride and ammonia, and washed with the same liquid without interruption until potassium ferrocyanide can no longer be recognised in the filtrate after acidulation.

The hydroxides are then treated with hydrochloric acid, in which they dissolve completely if the above-mentioned operations have been correctly carried out. If there remains an insoluble residue of ferrocyanide it must be washed and again treated with potassa-lye, as above directed.

The solution of the metallic chlorides which no longer contain phosphoric or arsenic acid, if the precipitated ferrocyanides have been well washed, is concentrated if necessary, the greater part of the free acid is neutralised with ammonia; the liquid (still clear) is mixed with ammonium carbonate in moderate excess, allowed to stand for some time; the ferric hydroxide which remains undissolved is filtered off, washed with water containing a little of the filtrate with the addition of the washings, heated in order to expel the chief part of the ammonium carbonate, acidified with hydrochloric acid—whereby the yellowish flocculent precipitate formed on boiling, and containing a part of the uranium, is re-dissolved—and the copper remaining in the solution is precipitated with sulphuretted hydrogen with the application of heat. The copper sulphide was always obtained free from uranium. The liquid filtered from the former is concentrated, the uranium precipitated with ammonia, and the precipitate of uranium hydroxide is converted into uranic-uranous oxide by ignition in an uncovered crucible, and weighed as such. As a check-experiment, it is then converted into uranous oxide by ignition in a current of hydrogen, and the weight is again determined.—*Zeitschrift für Analytische Chemie*, xxxiv., p. 437.

NOTICES OF BOOKS.

Kurzes Handbuch der Kohlenhydrate. (II. Band). By B. TOLLENS. Breslau: E. Trewendt. 1895.

MODERN chemistry is like modern music in acknowledging more and more the sway of the *leit-motif*. Reading the history of the science backwards, it is always easy to give a "too, too solid form" to that which is only a ghostly presence; in other words, to discover the dominant theory of a period long before it existed. But in dealing with the forward movement of our own present time, the ordering and systematising of the group of carbohydrates, there is no doubt that the results in this case are begotten of the theory. Nor could there be any better exemplification of the character of the movement than a careful comparison of the volume before us with its predecessor (I. Band, 1888), of which it is a substantial amplification, and in some respects a revision. The *leit-motif*, it is hardly necessary to premise, is the theory of the asymmetrical satisfaction of the four combining positions of the C-atom; this, as the basis of the "new isomerism," which specially characterises the carbohydrates.

Nor is it necessary to make more than a passing allusion to the "Seer" of the movement. Emil Fischer's position in relation to the subject-matter of the book is duly recognised in the author's preface. His work as a pioneer investigator has about it, we may remark, much that is unique. For while it has undoubtedly carried with it a number of discoveries of compounds and methods, with perhaps the attendant stimulus of novelty, its main purpose was the laborious verification of a strictly mathematical or geometrical forecast. Such "high academical" work is rare in our science, and it has a moral aspect which ought to give pause to those who talk lightly of "*fin de siècle* evolution."

We may contrast the "sugar movement" with the great development which preceded it—the chemistry of the aromatic series. This involved the elaboration of an equally striking chapter in isomerism, but the principles were in this case evolved *a posteriori*. The "inwardness" of this movement, moreover, centred in large measure round the peculiar, but extrinsic, attractiveness of the particular compounds which were brought to light with a prolific fertility. No one so far as suggested any striking development of art or industry as likely to follow from the discovery of the thirteenth hexanpentolal. Still, the melancholy conclusion that "there may be no money in it after all"—a finally destructive argument in many spheres of activity—would have had no more deterrent effect upon the pursuit of this particular No. 13 than it has had in damping the ardour of North Pole enthusiasts.

But, to the book. The author needs no introduction to English chemists. His researches in special chapters of the now great volume of carbohydrate chemistry are well known; and his contribution of experimental methods has been especially valuable. No one will question his qualifications for the task of chronicler of the movement in which he has taken so active a part, and, with the two monographs which he has produced before us, we are justified in saying the work could not have been in better hands. A preliminary idea of the scope and magnitude of the present volume (Part II.) will be gathered from the fact that there are over 1200 references to original papers. The systematic arrangement of the subject-matter is necessarily based upon the classic work of Fischer, of which the Maestro himself has given a comprehensive digest in his papers entitled "*Synthesen in der Zuckergruppe*" (*Berl. Ber.*, 1890, p. 2114; 1894, p. 3189). The general relationships of the group, as disclosed by systematic synthesis and dissection (*Abbau*), the broader questions of constitution, and the more refined conclusions as to configuration, are dealt with in a preliminary section, which also includes a general account of the more special characteristics of the group, e.g., optical

properties, thermal constants, fermentation, and other hydrolyses. This section is admirably condensed into 55 pages of the text. Candidates for competitive examinations will rejoice in the prospect hereby afforded of "getting up" this great subject in the compass of, say, one evening!

The table of genealogical descent of the typical hexoses, *d*-glucose and *d*-fructose, from formaldehyd, acrolein bromide, and glycerin, will appeal with force to the "cram" school of students. In the more serious view, it affords an excellent perspective of a whole campaign of methodical struggle. We will not, however, discuss the author's preamble according to its "location," but, to follow an excellent precedent, after the encyclopædic portions of the work have been noticed. In dealing with this, the experimental subject-matter, the author follows the received order:—(a) The carbohydrates proper (aldoses and ketoses) are dealt with as mono-, di-, and tri-saccharides, *i.e.*, generally the crystallisable sugars, in order of molecular weight, and lastly, the poly-saccharides; (b) the mannites or mannitols, or corresponding alcohols; (c) derivatives of the cyclic hexamethylene (inosite, quercite, &c.); and lastly, (d) the diversified group of saturated poly-hydroxy-acids derived from, or constitutionally related to, the carbohydrates.

There is little to be said in criticism of these sections. It is difficult to see how the work could have been more carefully done. To have selected the subject-matter from over 1200 original papers, and reproduced their essential features in 300 pages of text, is an invaluable effort of digestion and concentration. Specialists will possess themselves of the book at once, as a matter of course, and their judgment of its value will not be influenced by "these presents"; nor would its value as a work of reference be materially lessened by any objections on points of detail. Those who are not specialists can afford to believe in a few substances of doubtful identity, and accept some conclusions which they may have to unlearn, without prejudice to the advantage of taking a categorical survey of a careful census of this well-marked province of chemical individuals.

Thus, on the doubtful side. Some of the conclusions as to the identity of isomaltose will, in view of Brown and Morris's recent work, require revision. The author's view of the molecular structure of cellulose may be summed up as that of an "acetal" union of unit C_6 -groups, against which there appears to be a good deal of experimental evidence. This particular section, which includes the ligno-celluloses, has an amorphous character. But so have the compounds themselves, and hence the "Cinderella" position they continue to enjoy. If we wished to be oracular, we should prophesy concerning this group of out-casts and the Twentieth Century.

It is evident that no useful purpose would be served by an examination in detail of the encyclopædic matter of the text. It is of necessity a compilation: no pains have been spared in the collection and ordering of the experimental material, and considering the difficulty of photographing an expanding group—if we may be allowed the simile—the author is very much to be congratulated on the result.

What is perhaps of greater moment is the general plan of the work as sketched in the preamble, which is, or aims to be, co-extensive with the present development of the subject. This we think is somewhat too narrow; possibly the author has circumscribed it with intention. Those who follow the literature of the subject are aware that it is overflowing in every direction into the province of the physiologist. In fact, the sugar chemist is *ex officio* a physiologist. Fischer himself having laid his structural foundations on the most purely academic lines, now finds unexpected relationships of configuration to both the constructive processes of assimilation and the destructive processes of hydrolysis and ferment re-solutions. Brown and Morris, in this country, have contributed a memoir of fundamental import upon the root problems of assimila-

tion. Tollens, also, and his students past and present, are doing valuable work in physiological problems.

Of course the inevitable consequence of exhaustive investigation of the carbohydrates is to open out the whole province of plant chemistry. But there are further consequences in view. The whole science of carbon chemistry is becoming involved. We have had a century of "pure chemistry." We have learned to treat matter as matter, with a respect which our mediæval ancestors failed even to anticipate. At this date we take Matter very much for granted (writing it with a capital M), and find our fascinations in problems of form. So far as these are purely geometrical they tend to finalities. Of course we could go on multiplying analogues to the end of time. But there enters the question of brain or mind exhaustion, and the antidote of new objectives. The new objective of organic chemistry is the chemistry of living organisms. We see its operation in all hands; there is no need to enforce the conclusion by demonstration. At the same time we do not feel "superfluous" in calling attention to this general convergence or divergence of research in connection with the subject of the book before us. As we have indicated, the author is sparing in his treatment of the physiological relationships of the subject-matter. The suggestive conclusions of Fischer, as to the relationships of assimilation and ferment resolutions to the configuration of the assimilating substance or ferment, are very sparingly noticed. There is no mention of the observations of A. J. Brown on the cellulose-forming properties of *Bacterium xylinum*. There are no special references to that most interesting problem presented by the natural history of the carbohydrates, *viz.*, the passage from saturated to unsaturated compounds. On the other hand, a glance at the Index will show that particular references to plant products are extremely numerous, and, as a knowledge of the author's researches, leaves us in no doubt as to his being a great student and patient investigator of the chemical problems of plant-physiology, we must conclude either that the plan of the work is not to admit of the discussion of physiological problems which is perhaps conveyed by the title, or that the task of dealing with these is deferred to a third volume.

If, therefore, the work in its present state of development leaves us with this one impression of shortcoming, it may be the result of a little *trop de sèle* on our part. Still we can all of us afford to be a little over-zealous when not engaged in putting ourselves "on record"; and it will be well if our teachers will put all their spare enthusiasm into a definite shaping of the careers of promising students towards the new fields of investigations now opening up.

Prof. Tollens's work is perhaps too strictly academical to be directly suggestive of fruitful subjects of research. But with the interpretations and forecast of the teacher it cannot fail to exert a most valuable influence in furthering the progress of the newest "New Chemistry," which is the chemistry of the plant cell.

Justus von Liebig: His Life and Work (1803 to 1873).

By W. A. SHENSTONE, F.I.C., Lecturer on Chemistry in Clifton College. Small 8vo., pp. 220. London, Paris, and Melbourne: Cassell and Co., Limited. 1895.

MR. SHENSTONE is right. Though not a quarter of a century has elapsed since Justus von Liebig joined the majority, and great as had been his services to Science and to the most useful of all the Arts, he is, save in scientific and technical circles, nearly forgotten. Our author mentions two instances showing how little he is known even among the "educated and respectable" classes. One current notion is, that Liebig was a man who gained a large fortune by making "extract of meat." Others think they have heard his name mentioned in connection with agriculture. A very common mistake is the notion that Liebig's father was a pharmacist, and that

the great luminary of Giessen and Munich himself was brought up to the same career. He had certainly been placed for a short time with an "apothecary," or, as he would be termed in England, a "chemist and druggist;" but after ten months his non-pharmaceutical experiments proved so alarming that his master was glad to get rid of him.

The work before us deals not so much with Liebig's private life as with his career and his influence upon Germany and upon the world. But there is one point to which attention cannot be too forcibly and too frequently drawn. In the earlier part of the century in Germany—as it is still to a deplorable extent in Britain—the mental calibre of a youth was judged solely by his power of assimilating the "classics," of remembering long strings of rules and exceptions, and of playing with "longs and shorts." Liebig had little verbal memory, and no taste for word-mongering. Hence he was denounced as a dunce, likely to be a disgrace to his teachers and his parents. What an instructive mistake! The classical scholars who were considered so greatly his superiors have passed, leaving the world no wiser than they found it, whilst Liebig has bequeathed to future generations a solid inheritance of research which is still continuing to grow and to bear fruit.

After an Introduction, and an account of his friendship for Woebler and of their joint researches, the author goes on to describe Liebig's discoveries in pure chemistry, his relations with Dumas,—which were not uniformly harmonious,—his acceptance of the fruitful doctrine of substitution, his researches on fermentation—involving a dispute with Pasteur, of which Mr. Shenstone speaks perhaps too favourably. We have then his epoch-making contributions to the chemistry of agriculture and to physiological chemistry.

A special chapter is worthily devoted to his educational work. To him, more perhaps than to any other man, is due the splendid upburst of intellectual life which has made the German universities foci of discovery, and has even contributed powerfully to the development of German manufacturing industry. It has been said that the first Napoleon was able to "spit" generals. In like manner it may be said that Liebig could "spit" discoverers, inventors, professors, full of originality and carrying on the work of their great master.

Liebig's "Familiar Letters on Chemistry" are not overlooked. It is very truly said that these letters "had much to do with the present intelligent attitude of the German 'practical man' towards Science, which has contrasted so strangely with that of his average English brother for many years past, much, it is to be feared, to the material disadvantage of the latter." The German has learnt that, to ensure manufacturing superiority, abundant capital, business tact, and energy are not sufficient without a knowledge of the scientific principles on which the various industrial arts are based.

Mr. Shenstone deserves hearty thanks for the production of a work so opportune and so useful.

A Short Manual of Analytical Chemistry, Qualitative and Quantitative, Inorganic and Organic: following the Course of Instruction given in the South London School of Pharmacy. By JOHN MUTER, Ph.D., F.R.S.E., F.I.C., &c.; Analyst to the Metropolitan Asylum Board; Public Analyst for Lambeth, Wandsworth, Southwark, Newington, Rotherhithe, and the Lindsey Division of Lincolnshire; Past President of the Society of Public Analysts; late Editor of the *Analyst*. Sixth Edition, illustrated. London: Simpkin, Marshall, Hamilton, Kent, and Co. (Limited); and Baillière, Tindall, and Cox. 1895.

THE work before us, though primarily intended for the guidance of pharmaceutical students, will be found widely useful. Setting out with a view of the processes employed by practical chemists, the author proceeds to the

detection of the metals in which cerium is included, though indium, rhodium, thallium, and uranium are omitted, doubtless as not being used in medicine.

Next follow methods for the detection and separation of the acid radicles, the qualitative analysis of mixtures of unknown salts, the qualitative detection of alkaloids of some other organic substances used in medicine, and a general sketch of procedure in toxicology.

Successive chapters treat of weighing, measuring, and specific gravity, no notice being taken of the very useless hydrometer of Beaumé. Next follow instructions for volumetry and the use of the nitrometer, the gravimetric determination of metals and acids, for the determination of phosphates in soils and manures, and for the full analysis of the organic matters in potable waters. Instructions are given in ultimate organic analysis, the nitrogen being determined according to the processes of Dumas, of Varentrapp, and of Kjeldahl.

In Chapter X. there are given special processes for the sanitary examination of waters, of air, and of the more usual articles of food. Referring to Pepper, we cannot help asking why the importation of "poivrette" is still permitted? Special processes are laid down for the analysis of the more important drugs, of urine, and urinary calculi.

In the concluding chapter there are instructions, necessarily rather brief, for gas analysis—now of rapidly increasing importance—and of polariscopic and spectroscopic analysis. The section on the analysis of urine is enriched with illustrations, showing the microscopic aspects of pus, micrococci, uric acid, cystin, blood discs, triple phosphates, &c.

Dr. Muter's work is, in short, a useful work of reference.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxi., No. 15, October 7, 1895.

An Ascent to the Summit of Mont Blanc, and on the Researches Executed during the Summer of 1895.—J. Janssen.—The author has studied the presence of watery vapour in the atmospheres of the sun. The spectrum was entirely deprived of its rays of an aqueous origin; all the group near D was absent, as well as that of C; it was so pale that it was difficult to decide if it was in its place. It was evident that on another step every aqueous manifestation would have disappeared.

Study of certain Meteorites.—Henri Moissan.—The author has resumed the study of certain metallic or holosideric meteorites in consequence of the discovery of a transparent diamond in the meteorite of Cañon Diablo. He arrives at the following conclusions:—In some holosideric meteorites there is no carbon; in others we find either amorphous carbon, or a mixture of this variety and of graphite. In a single meteorite, that of the Cañon Diablo, the author has found together the three varieties of carbon—diamond (black and transparent), graphite, and amorphous carbon.

Inflammability of "Fire-damp."—R. L. Devaux proposes to annul the inflammability of "fire-damp" by an admixture of carbon dioxide.

Mechanical Properties of the Alloys of Copper and Zinc.—Georges Charpy.—This paper can scarcely be regarded as a chemical communication. The most advantageous alloys are those containing from 30 to 43 per cent of zinc, and their value then diminishes rapidly. The elongation before rupture also increases with the proportion of zinc, and then decreases rapidly.

Glucinum Carbide.—P. Lebeau.—On heating in the electric furnace a mixture of glucinum oxide and of coke we have obtained, not the metal, but a definite carbide. Pure glucina was intimately mixed with half its weight of sugar charcoal. The mixture was agglomerated with a little oil and compressed into the form of small cylinders, which were then heated to incipient redness. The cylinders were then introduced into a tube of coke, closed at one end, and arranged in such a manner that the mixture was in the hottest part of the furnace. The current employed was of 950 ampères and 40 volts. The experiment required from eight to ten minutes. In a series of experiments with a current of 350 ampères and 50 to 60 volts, there was only obtained a nitride, or products containing nitrogen and carbon. Pure glucinum carbide appears in the form of yellowish brown microscopic crystals presenting hexagonal facets. It easily scratches quartz, and its specific gravity at 15° is 1.9. Chlorine attacks it readily at a dull red heat, forming a volatile chloride and a black residue of amorphous carbon and graphite. Bromine reacts at a rather higher temperature, and iodine has no action at 800°. Pure oxygen at dull redness produces a superficial oxidation. Vapour of sulphur reacts below 1000°, forming a sulphide. Phosphorus and carbon have no apparent action at dull redness. The composition of the carbide appears to be C_3Be_4 . The atomic weight of glucinum should be close upon 14, and glucina should be a sesquioxide, Be_2O_3 .

Researches on the Combinations of Mercury Cyanide with the Iodides.—Raoul Varet.—A thermochemical paper not of sufficient importance to warrant its insertion in full.

Double Decompositions ensuing between Mercury Cyanide and the Alkaline and Alkaline-earth Metals.—Raoul Varet.—The fluorides, chlorides, sulphates, nitrates, carbonates, acetates, and picrates of these metals do not undergo double decomposition with mercury cyanide. With the bromides there is a slight double decomposition. With the iodides there is double decomposition, regulated by the production of the triple salts $HgCy_2$, MCy_2 , Hgl_2 . With the sulphides there is complete double decomposition.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xiii.-xiv., No. 12, 1895.

Certain Derivatives of the Bromides in C_3 .—R. Lespiau.—An account of 1.2.3-tribromopropane; of 1.3-dibromopropane; of 1.3.3-tribromopropane oxymethane; 1.2-dibromopropene oxymethane; and 1-bromopropene oxymethane.

Benzinesulphoorthotoluidine and some of its Derivatives.—Ch. Rabout.—We see the great resistance of this sulphamide to oxidation, and its great stability in heat to the presence of dilute acids, notwithstanding its amidic character.

Determination of Organic Nitrogen by the Kjeldahl Process, in the absence of Nitrates.—H. Causse.

Volatile Acidity of Wines.—H. Jay.—The proportions of volatile acids found in French and Spanish wines of reliable origin oscillates between 0.38 and 0.80 gm. per litre, calculated as monohydrated sulphuric acid. On the contrary, all the Algerian wines which have been submitted to me contain per litre at least 1.30 grms., and in a majority of cases exceeding 1.60 grms.

Determination of Volatile Acids in Wines.—E. Burcher.

No. 13.

New Tube for Fractionated Distillations Modified by M. Lebel.—G. Berlement.—This apparatus cannot be described intelligibly without the accompanying figure.

New Researches on the Combination-heats of Mercury with other Elements.—Raoul Varet.—The heat disengaged in the combination of mercury with gaseous chlorine is +53.3 cal.; with liquid bromine, +40.6; with iodine, solid, +25.2 cal. (for the red compound) and 22.2 cal. (for the yellow compound); with oxygen, gaseous, +21.5 cal.

Isomeric Transformations of the Mercury Salts.—Raoul Varet.—A list of the heats developed by the mercurial compounds in their respective transformations.

Separation of Lime from Strontia and Baryta.—J. Dupasquier.

Action of Halogens on Methylic Alcohol.—A. Brochet.—This paper is not adapted for useful abstraction, and cannot claim insertion *in extenso*.

Preparation of the Amines of the Fatty Series.—A. Trillat.—The author gives an account of the preparation of monomethylamine, of the action of ammoniacal salts upon formaldehyd, the influence of reduction on the preparation of ethylamine.

Recognition of Alum in Wines.—M. Georges.—The author proposes the two following solutions:—1. Solution of pure tannin—Pure, 3.40 grms.; distilled water to make up 100 c.c. Each c.c. of this solution precipitates 0.005 gm. alumina, *i.e.*, the quantity contained in 0.0463 gm. of alum. 2. Solution of sodium acetate—($C_2H_3NaO_2 \cdot 3H_2O$) or ($C_2H_3NaO_2 \cdot 3H_2O$); neutral sodium acetate, crystalline, 24 grms.; distilled water to make up 100 c.c. Each c.c. of this solution contains a weight of combined acetic acid corresponding to 0.10 gm. monohydrated sulphuric acid. The author measures 20 c.c. of wine into a wide test-tube, and adds 2 c.c. of the solution of tannin. After agitation, he pours into the mixture 3 c.c. of the solution of sodium acetate, stirs again, and then leaves the mixture to settle, observing the phenomena produced. If, after five minutes, there appears a clotty precipitate we may assert the presence of alum. If the wine remains clear, or is at most slightly cloudy, the wine is genuine, or contains less than 1 decigram. of alum per litre.

Existence of a Sulphuretted Substance in Cotton Oil.—J. Dupont.—American food-fats containing cotton oil have often become rancid, and in that state have a deceptive action with the silver nitrate. The author distils cotton-oil in a strong current of steam. The water collected has a disagreeable smell of a sulphuretted product. On successive treatments with ether there is obtained a small quantity of an oily matter which is attacked in the water-bath with nitric acid and potassium chlorate. If the excess of acid is driven off and the residue taken up in water the addition of barium chloride determines a strong precipitate of barium sulphate.

Use of Superphosphates.—Jules Joffre.—The author's experiments warrant the conclusion that the preferable action of superphosphate is not merely due to a more thorough dissemination in the soil, but to absorption of a part of the phosphoric acid in the state of compounds soluble in water. There is no proof that reverted phosphoric acid exists in the soil in the state of tricalcic phosphate.

Exposition of some Points concerning the Analysis of Fatty Substances.—G. Halphen.—The author gives, firstly, an examination of the physical characteristics, specific gravity, viscosity, spectroscopic behaviour, polarisation, solubility, congelation, expansion, and elastic conductivity. The physical methods just enumerated are not of themselves sufficient. Among the chemical methods, it is pointed out that Fauré's test, the action of chlorine gas, is not decisive; some vegetable oils are not bleached by this reagent, but turn brown; whilst some animal oils, especially that of the feet of horses, are blackened. The Welman's test and the phosphoric acid method are not trustworthy.

MISCELLANEOUS.

Hygienic Decision on Potable and Household Waters.—Prof. Flüge.—At the General Meeting of the German Association for the Care of Public Health, Prof. Flüge put forward the following propositions:—1. The customary hygienic decision on waters simply on the basis of a chemical, bacteriological, and microscopic examination of samples sent, is in almost every case to be rejected. 2. A single examination of water as to its admissibility for drinking or domestic consumption must, above all things, be followed by a visit of inspection to the place where the sample was taken. In many cases this examination alone leads to a conclusion that it may be supplemented by macroscopic inspection, and a determination of the hardness and the iron. In new installations the freedom of the water from micro-organisms should be ascertained. 3. The hygienic significance of remarkable analytical results can be generally ascertained only by repeated inspection and examination.—*Zeit. f. Angewandte Chemis.*

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THE CHEMICAL NEWS.

VOL. LXXII., No. 1875.

NOTE ON THE REDUCTION OF THE OXIDES OF IRON BY MEANS OF CARBON MONOXIDE.

By ISAAC BRAITHWAITE.

FERRIC oxide, formed by igniting the precipitated hydrate, in granular powder which would pass through a sieve of 18 meshes to the inch, but not through one 28 to the inch, was heated in a porcelain tube to a low red heat. Successive small portions of CO were passed over it, each portion being passed back and forward repeatedly (from ten to twenty times) during a period of about five minutes (in some cases much longer). The proportion of CO₂ in each portion was determined by absorption in potash and weighing. This was repeated until the oxide was completely reduced to metallic iron. The results were not sufficiently accordant to warrant the giving of exact figures. Probably this may have arisen from several causes. The temperature may not have been sufficiently uniform, although one or two direct experiments showed no marked change in the results when the temperature was raised considerably above that usually adopted. The CO employed was not quite pure, and probably varied a little. The time during which each portion was allowed to act certainly affected the results; the most accordant ones being obtained when the action was prolonged many hours; but as some hundreds of successive portions were used, it was impracticable to allow so much time for each.

The facts ascertained may be stated generally thus:—At a low red heat, in presence of excess of Fe₂O₃, CO is completely (or almost completely) oxidised to CO₂. With excess of Fe₃O₄, rather more than two-thirds is oxidised to CO₂, the resulting mixture of gases being nearly CO + 2CO₂. With excess of FeO, about one-third is oxidised, leaving the mixture nearly 2CO + CO₂. When the iron is completely reduced, if the temperature falls below a dull red heat, there is considerable formation of CO₂ and deposit of carbon, probably from the formation and decomposition of iron carbonyl. The experiments were reversed by passing CO₂ over iron, and the action was proved to be reversible; that is, CO₂ passed over red-hot iron became two-thirds reduced; over FeO, one-third reduced; over Fe₃O₄, not reduced at all.

I am indebted to Mr. S. R. Rowling for the carrying out of these experiments.

A NEW FORM OF ACCUMULATOR.

By H. N. WARREN, Research Analyst.

THE invention relates to accumulators of a special type, whereby an extraordinary large surface of material is exposed. The negative element, consisting of a plate of pure porous lead, is manufactured for the purpose by partial compression in suitable moulds of spongy lead obtained by the slow precipitation of lead from a solution of the acetate by means of zinc; around this is compressed, again, an intimate mixture of metallic lead and litharge, made by melting lead in a deep clay crucible, and introducing into the same about 40 per cent of litharge, the whole being well stirred until cold. By this means a thorough incorporation of the litharge is obtained, the metallic appearance of the lead present being entirely masked. The metallic lead as produced in the first in-

stance, together with the litherode lining, is tightly compressed into thin flat porous pots, each plate thus forming one negative element. For the construction of the positive plates is prepared an intimate mixture of lead peroxide, by first incorporating with the lead, as in the former instance, instead of litharge, barium carbonate; the resulting granular powder thus obtained being afterwards freed from the barium carbonate by digesting the same in hot hydrochloric acid, thus leaving the lead in a state of purity, which is afterwards mixed with a sufficiency of the plumbic peroxide and used as a charge for the positive cell, or to constitute, in other words, the positive plate. The resistance in such accumulators is very small, whereas at the same time they compare more favourably with others as regards their amperage. Plates of this description are now to be obtained at most of the leading electricians, and will be found highly beneficial to those requiring to demonstrate the practical construction, and at the same time the charging, of accumulators to classes or others; being rapidly charged by small batteries, and retaining the current admirably.

Liverpool Research Laboratory,
18, Albion Street, Everton, Liverpool.

ON THE DETERMINATION OF ARGON.

By Th. SCHLESING, Jun.

SINCE argon has been discovered the question has been raised whether, like the other elements of the atmosphere, it interferes in the phenomena of life.

The experiments hitherto made on this point have given negative results. G. McDonald and A. M. Kellar have sought for argon in the composition of certain animals and certain seeds, but they have not met with it in an appreciable quantity. Nevertheless the subject is not exhausted, and it will doubtless be further examined, especially if argon plays a part in vegetable synthesis. For such a study it may be useful to determine with precision the argon contained in a given atmosphere. I have attempted this determination, to which I have been the more attracted because, independently of any physiological research, the determination of argon applied to normal air is doubtless of interest.

In consequence of its rarity we are naturally led to determine argon in very large volumes of air. But the measurement in the manifestation of large volumes of gases generally involves bringing them in contact with water, whence there result nearly always sensible errors. It is possible to obtain good results by operating only on volumes of air corresponding to 1·5 litres of nitrogen, and effecting all the measurements over mercury. We then employ for the separation of argon and nitrogen a system of apparatus of limited capacity, when it becomes easy to produce a vacuum, as well before the introduction of the gas to be measured as after its extraction, which constitutes a most precious resource.

After the example of Lord Rayleigh and Prof. Ramsay, to isolate the argon contained, *e.g.*, in normal air, I absorb the nitrogen of the air by means of magnesium after having eliminated the oxygen and the carbonic acid.

The arrangement for this purpose cannot be described intelligibly without the accompanying figure. The author's procedure has been carefully verified.

It has been enquired if argon treated in this manner is sufficiently purified. To ascertain this point I have taken specimens of the gas obtained in the determinations. Oxygen has been added, and the mixture has been submitted to the action of the spark in presence of potassa for eight hours. The oxygen has then been eliminated by means of pyrogallol and the gaseous residue measured anew. I have, *e.g.*, found:—Initial volume, 15·796 c.c.; final volume, 15·802 c.c. The difference is very small, and is of the degree of the errors of measurement.

I have made a global verification (so to speak) of the procedure. I prepared chemical nitrogen by passing over copper and copper oxide, at a red-heat, nitrous oxide obtained by the decomposition of ammonium nitrate. I measured this nitrogen after having added an accurately estimated volume of argon obtained from a determination conducted on my method. The proportions of the two gases was of the same degree as in the atmosphere. The mixture has undergone all the operations and manipulations indicated. I compared the volume of argon introduced to that of the argon recovered. Three experiments of this kind gave :—

Gaseous mixture introduced.			Percentage of the Argon introduced.	
Argon.	Chemical Nitrogen.	Argon recovered.	Loss. Total.	
1. 18.138 c.c.	1395.6 c.c.	18.008 c.c.	0.130	0.72 c.c.
2. 18.155 "	1409.2 "	18.083 "	0.072	0.40 "
3. 16.936 "	1288.1 "	16.809 "	0.127	0.75 "

These figures give an idea of approximation obtained. I shall return to the cause of the small loss observed, and give an account of the determinations effected both of normal air and of other gaseous mixtures, such as those extracted from the soil. At present I will merely say that normal air yielded as a mean (number obtained without correction) 1.183 vol. of argon to 100 vols. of atmospheric nitrogen (nitrogen and argon), or 0.935 vol. to 100 vols. air, figures which approximate in deficiency to less than 100 of their value.—*Comptes Rendus*, cxxi., p. 525.

DETERMINATION OF HEAVY METALS BY TITRATION WITH SODIUM SULPHIDE.

By G. NEUMANN.

It is known that most alkaline metals are precipitated quantitatively from their solutions by an alkaline sulphide. This reaction is utilised by mixing the metallic solution in question with a known excess of the precipitant, and titrating back the excess of sulphide. As the alkaline sulphides have an alkaline reaction, we might expect that the object might be attained without using an excess of alkaline sulphide by taking litmus or phenolphthalein as an indicator as in the titration of acids. Experiments in this direction, however, proved useless, since alkaline sulphides, like hydrogen sulphide, destroy the colour of the indicator.

On this account the neutral metallic salt to be analysed was placed in a measuring flask along with a considerable excess of a dilute standardised solution of an alkaline sulphide, and the flask was filled up to the mark with water. As the precipitates formed are sometimes not very dense and do not readily subside, there was added in most cases a 20 per cent solution of sodium chloride before filling up to the mark, and the liquid well shaken and thus quickly clarified. An aliquot part of the clear liquid was boiled with a measured excess of decinormal sulphuric acid until the vapour on being tested with moist lead paper was found free from hydrogen sulphide, and was then titrated back with decinormal potassa, using phenolphthalein as an indicator. The quantity of metal originally present may then be calculated. An example may explain these general indications. For standardising the sodium sulphide there were taken decinormal potassa, (?) decinormal sulphuric acid. 17.1 c.c. of the solution of sodium sulphide was boiled with 30 c.c. sulphuric acid until all sulphuretted hydrogen was expelled, and used with phenolphthalein as indicator, 11.8 c.c. potassa for neutralisation, whence the sodium sulphide was calculated as 1.05/10 normal.

With this solution we titrated, e.g., 1/5 normal solution of potassium chrome alum. 25 c.c. of this liquid were mixed in a 200 c.c. flask with 20 c.c. of a 20 per cent

solution of sodium chloride and 50 c.c. of the above solution of sodium sulphide, and filled up to the mark. After shaking up the contents of the flask, green chromium hydroxide quickly subsided. 50 c.c. of the liquid were poured through a folded filter and boiled with 5 c.c. of sulphuric acid until the complete expulsion of the sulphuretted hydrogen, and titrated back with 4.8 c.c. potassa.

From these data there was calculated a proportion of 0.526 per cent Cr_2O_3 as against 0.51 per cent theoretically.

The author has shown that the method is widely applicable, as he has made experiments with ordinary alum, potassium-chrome alum, ferro-ammonium sulphate, ferric chloride, manganese-ammonium sulphate, nickel ammonium sulphate, cobalt, zinc, and copper sulphates, lead and silver nitrates, and cadmium sulphate.

With metals, the sulphides of which are readily separated in a granulated state, the addition of sodium chloride was sometimes omitted. In some metals, the salts of which are precipitable by sulphuretted hydrogen in an acid solution, and those, such, e.g., as copper, form colloidal sulphides on the addition of sodium sulphide, the separation of the sulphide was effected by the addition of an acid. The analysis was then effected by heating the mixture of metallic salt and sodium sulphide in a measuring flask with a measured excess of sulphuric acid until the reaction of sulphuretted hydrogen no longer appeared, filling up to the mark when cold and titrating a filtered aliquot part with potassa. The author has applied this method in determinations of lead as well as of copper.

The method is of course only applicable if the salts under examination are neutral. If acid the free acidity must be expelled prior to titration. Most chlorides lose their excessive hydrochloric acid if they are dried up on the water-bath, taken up in alcohol and again dried. Such experiments were effected with an acid solution of zinc and copper. Here a three-fold evaporation with alcohol at 97 per cent was the most favourable. After a fourth evaporation from alcohol, the residue did not yield a clear solution. The evaporation is effected very rapidly if air is blown upon the surface of the liquid. Sulphates are previously converted into acid chlorides by treatment with barium chloride and hydrochloric acid. This is best effected in a measuring flask, and an aliquot part is then drawn off with a pipette as above described.

Nitrates must be twice evaporated down with concentrated hydrochloric acid, and then made neutral as already described.—*Zeitschrift für Analyt. Chemie*, xxiv., p. 454.

ON THE VAPOUR-TENSIONS OF MIXTURES OF VOLATILE LIQUIDS.*

By C. E. LINEBARGER.

(Continued from p. 196).

Experimental Results with Mixtures of Normal Liquids.

In the following Tables (II. to IX.) are given those data of the experiments necessary for the calculation of the vapour-tensions. The superscriptions over each column of data render any preliminary mention here unnecessary.

Relations between the Vapour-tensions, Partial and Total, and the Concentration of the Liquid Phases.

We remark first, that the tension of the mixed vapour emitted by any of the mixtures of volatile liquids examined is always greater than the tension of the less volatile liquid and always less than that of the more volatile liquid; also, that the partial tension or pressure

* Abridged from the *Journal of the American Chemical Society*, vol. xvii., No. 8, August, 1895.

TABLE II.—Vapour-Tensions of Mixtures of Benzene and Monochlorobenzene at 34°8'.

Vapour-tension of Benzene at 34°8' is 145·4 m.m. of Mercury.
Vapour-tension of Chlorobenzene at 34°8' is 20·3 m.m. of Mercury.

Mols. C_6H_5Cl in 100 mols. of liquid mixture.	Mols. C_6H_5Cl in 100 mols. of gaseous mixture.	Grms. C_6H_5Cl in vapour.	Grms. C_6H_6 in vapour.	Tension of C_6H_5Cl in m.m.	Tension of C_6H_6 in m.m.	Volume of air in m.m.	Barometer in m.m.	Internal pressure in m.m.
15·18	1·33	0·0454	2·3075	1·7	124·6	3782	763	11
29·08	6·11	0·0857	0·9143	6·6	101·3	1900	757	17
65·06	19·37	0·1800	0·5202	12·3	51·3	2032	758	18
79·21	35·15	0·3572	0·4750	19·1	27·9	3787	756	12

TABLE III.—Vapour-Tensions of Mixtures of Toluene and Monochlorobenzene at 34°8'.

Vapour-tension of Toluene at 34°8' is 46·8 m.m. of Mercury.
Vapour-tension of Chlorobenzene at 34°8' is 20·3 m.m. of Mercury.

Mols. C_6H_5Cl in 100 mols. of liquid mixture.	Mols. C_6H_5Cl in 100 mols. of gaseous mixture.	Grms. C_6H_5Cl in vapour.	Grms. C_6H_5 in vapour.	Tension of C_6H_5Cl in m.m.	Tension of C_6H_5 in m.m.	Volume of air in c.c.	Barometer in m.m.	Internal pressure in m.m.
18·96	9·84	0·0510	0·3821	4·3	38·2	1963	757	17
41·82	22·66	0·0985	0·2754	8·1	27·6	1973	760	21
76·71	67·79	0·2089	0·0821	17·5	8·2	1965	757	18

TABLE IV.—Vapour-Tensions of Mixtures of Benzene and Monobromobenzene at 34°8'.

Vapour-tension of Benzene at 34°8' is 145·4 m.m. of Mercury.
Vapour-tension of Bromobenzene at 34°8' is 8·0 m.m. of Mercury.

Mols. C_6H_5Br in 100 mols. of liquid mixture.	Mols. C_6H_5Br in 100 mols. of gaseous mixture.	Grms. C_6H_5Br in vapour.	Grms. C_6H_6 in vapour.	Tension of C_6H_5Br in m.m.	Tension of C_6H_6 in m.m.	Volume of air in c.c.	Barometer in m.m.	Internal pressure in m.m.
30·33	24·30	0·0395	0·4975	2·6	103·1	1018	757	13

TABLE V.—Vapour-Tensions of Mixtures of Benzene and Chloroform at 34°8'.

Vapour-tension of Benzene at 34°8' is 145·4 m.m. of Mercury.
Vapour-tension of Chloroform at 34°8' is 289·2 m.m. of Mercury.

Mols. $CHCl_3$ in 100 mols. of liquid mixture.	Mols. $CHCl_3$ in 100 mols. of gaseous mixture.	Grms. $CHCl_3$ in vapour.	Grms. C_6H_6 in vapour.	Tension of $CHCl_3$ in m.m.	Tension of C_6H_6 in m.m.	Volume of air in c.c.	Barometer in m.m.	Internal pressure in m.m.
16·97	24·30	0·3243	0·6607	39·6	123·5	1032	755	25
50·53	63·74	1·1513	0·4187	130·7	74·3	1030	756	25
59·47	73·25	1·4770	0·3531	162·2	59·2	1030	749	25

TABLE VI.—Vapour-Tensions of Mixtures of Toluene and Chloroform at 34°8'.

Vapour-tension of Toluene at 34°8' is 46·8 m.m. of Mercury.
Vapour-tension of Chloroform at 34°8' is 289·2 m.m. of Mercury.

Mols. $CHCl_3$ in 100 mols. of liquid mixture.	Mols. $CHCl_3$ in 100 mols. of gaseous mixture.	Grms. $CHCl_3$ in vapour.	Grms. C_6H_6 in vapour.	Tension of $CHCl_3$ in m.m.	Tension of C_6H_6 in m.m.	Volume of air in c.c.	Barometer in m.m.	Internal pressure in m.m.
28·74	65·29	0·4856	0·1994	64·7	34·4	1040	747	24
60·43	89·20	1·3578	0·1270	160·9	19·5	1031	754	23

TABLE VII.—Vapour-Tensions of Mixtures of Benzene and Carbon Tetrachloride at 34°8'.

Vapour-tension of Benzene at 34°8' is 145·4 m.m. of Mercury.
Vapour-tension of Carbon Tetrachloride at 34°8' is 169·4 m.m. of Mercury.

Mols. CCl_4 in 100 mols. of liquid mixture.	Mols. CCl_4 in 100 mols. of gaseous mixture.	Grms. CCl_4 in vapour.	Grms. C_6H_6 in vapour.	Tension of CCl_4 in m.m.	Tension of C_6H_6 in m.m.	Volume of air in c.c.	Barometer in m.m.	Internal pressure in m.m.
7·21	9·66	0·1741	0·8260	14·5	135·4	1205	762	18
18·68	20·54	0·3931	0·7561	32·5	125·5	1205	758	20
28·00	35·71	0·6267	0·5730	60·0	105·0	1016	756	12
50·19	55·03	1·1231	0·4666	91·3	75·6	1201	762	19
63·88	65·27	1·2699	0·3431	103·1	54·5	1219	760	27
77·89	83·01	1·5321	0·1669	117·6	31·8	1034	754	26

TABLE VIII.—Vapour-tensions of Mixtures of Toluene and Carbon Tetrachloride at 34°8'.

Vapour-tension of Toluene at 34°8' is 46·8 m.m. of Mercury.
Vapour-tension of Carbon Tetrachloride at 34°8' is 169·4 m.m. of Mercury.

Mols. CCl_4 in 100 mols. of liquid mixture.	Mols. CCl_4 in 100 mols. of gaseous mixture.	Grms. CCl_4 in vapour.	Grms. C_6H_6 in vapour.	Tension of CCl_4 in m.m.	Tension of C_6H_6 in m.m.	Volume of air in c.c.	Barometer in m.m.	Internal pressure in m.m.
30·69	58·19	0·4754	1·2046	51·5	37·0	1016	756	12
53·85	78·86	0·9305	0·1260	78·3	22·3	1022	758	17
60·00	83·67	0·9624	0·1126	99·1	19·4	1020	759	14
91·87	97·22	1·6063	0·0281	155·1	4·5	1017	756	13

TABLE IX.—Vapour-Tensions of Mixtures of Nitrobenzene and Carbon Tetrachloride at 34°8'.

Vapour-tension of Nitrobenzene at 34°8' is 1·16 m.m. of Mercury.

Vapour-tension of Carbon Tetrachloride at 34°8' is 169·4 m.m. of Mercury.

Mols. CCl_4 in 100 mols. of liquid mixture.	Mols. CCl_4 in 100 mols. of gaseous mixture.	Grms. CCl_4 in vapour.	Grms. $\text{C}_6\text{H}_5\text{NO}_2$ in vapour.	Tension of CCl_4 in m.m.	Tension of $\text{C}_6\text{H}_5\text{NO}_2$ in m.m.	Volume of air in c.c.	Barometer in m.m.	Internal pressure in m.m.
5·37	93·51	0·3095	0·0175	18·9	1·3	19·73	760	20
50·73	94·47	1·1111	0·0489	113·9	6·2	1020	756	12
73·54	96·09	1·4420	0·0471	141·5	5·6	1022	753	18
95·21	98·61	1·7798	0·0190	167·6	2·3	1022	753	18

of either component, of any mixture, is always less than the vapour-tension of the component in a state of purity;* these two properties belong to all the mixtures investigated. In the discussion of the other properties, we shall find it convenient to divide the mixtures into classes. In the first class we put the mixtures of benzene and toluene with monochlor- and monobrombenzene; in the second, the mixtures of chloroform with benzene, and with toluene; in the third, the mixtures of carbon tetrachloride with toluene, and with benzene; and in the fourth and last, the mixture of nitrobenzene and carbon tetrachloride.

Now the mixtures of the first class are made up of liquids which are very similar in their chemical constitution, and it is natural to expect that they will exhibit the very simplest phenomena when mixed with one another. And, indeed, this expectation is realised, for the vapour-tensions of their mixtures are seen to be linear functions of the concentration: in the graphic representations (abscissæ = molecular percentages; ordinates = vapour-tensions) of the determinations, these fall upon or very close to the straight lines connecting the points on the axes of ordinates corresponding to the vapour-tensions of each of the pure liquids. In order to find the vapour-tension of any mixture of these liquids, all that is necessary to do is to connect on the axis of ordinates, the points representing the vapour-tensions of the two liquids in a state of purity, by a straight line, and where the perpendicular to the axis of abscissæ cuts this line, the value of the ordinate corresponding to the point of intersection gives the vapour-tension of the chosen concentration; of course, partial tensions can be found in a similar way. Also, by the application of the "rule of mixtures," it is easy to calculate the total or partial tensions. It may be worth while to remark, in passing, that these four liquids, which we have put in a class by themselves, are just those which verify by far the best the generalisations of van der Waals; undoubtedly, these liquids are to be reckoned as in the highest degree "normal," as their behaviour approaches most nearly that theoretically predicted.

In the second of our classes we find a different behaviour. When chloroform is added to benzene or to toluene, the total vapour-tension is less than that resulting from the calculation by the rule of mixtures; the variation reaches a maximum when 100 molecules of the mixture contain from 50 to 60 molecules of chloroform; the curve then tends to approach the straight line connecting the points on the axis of ordinates representing the vapour-tensions of the pure liquids, practically coinciding with it when the number of chloroform molecules has passed 80. The depression of the vapour-tension of chloroform, caused by the addition of either benzene or toluene, is linearly proportional to the concentration only in solutions containing less than 20 molecules of either hydrocarbon to 100 molecules of the mixture.

When we consider the partial tensions of these mixtures, we see that the same regularity as was observed in the

first class of liquids is found here, but only for toluene and benzene; the partial tension curve for chloroform resembles closely in its contour that for the total tension of the mixture. The departure of chloroform from the straight line is not, however, very marked.

In the third class of mixtures we meet with a different behaviour. When benzene or toluene is added to carbon tetrachloride, we observe that the curve of total tension follows closely the line connecting the points corresponding to the vapour-tensions of the mixed liquids until towards the abscissæ value of 80; the curve then commences to fall, only to rise again, and pass above the straight line, when, finally, it changes its direction to fall upon the axis of ordinates at the point standing for the vapour-tension of the pure hydrocarbon, benzene, or toluene, as the case may be. As is seen, the curve has three turning points. The curve of the partial tension of the carbon tetrachloride resembles in every detail, in each mixture, that of the total tension; but once more it is observed that the partial pressure curve for the hydrocarbons is, so to say, a straight line. It is truly a remarkable result that in the mixtures which have such different total tension curves, the curve for these two liquids should turn out so simple. There is but little doubt that the above instances are sufficient to render very probable the assumption that this behaviour is general, and that in all binary mixtures made up of benzene or toluene, with any other volatile liquid whatsoever, the same normality in the behaviour as regards partial vapour-tension of these two hydrocarbons will be found. It is even possible to go a step farther, and claim that, inasmuch as in the mixtures of the first class, normality of the partial pressure was found in the case of each component of the mixture, this normality will persist in mixtures of the halogen compounds of benzene with any other liquids.

The fact that benzene and toluene possess "straight line" partial pressure curves will enable us to get reliable and important information as to the partial pressures of other liquids mixed with either of the hydrocarbons, from a knowledge of the total pressure of the mixtures; for all that is necessary to do is to draw, in the coordinate system adopted in this paper, the total pressure curve and a straight line from the point, representing, on the axis of ordinates, the vapour-tension of benzene at the temperature at which the determination has been made, to the foot of the opposite ordinate; the value of any ordinate comprised between these two curves gives, then, the partial pressure, to a very close approximation, of the other component of the mixture.

Furthermore, it is apparent that the partial tensions of either chloroform or carbon tetrachloride is the same when mixed in the same proportions with either benzene or toluene; the simplicity of the behaviour of the latter liquids permits of the free exhibition of the peculiarities in that of the former.

(To be continued).

* This observation does not seem to be confirmed in the case of the partial pressure of nitrobenzene in its mixture with carbon tetrachloride. This exception, however, I am inclined to attribute to experimental errors, which made themselves particularly felt in the investigation of mixtures of these two liquids. Indeed, if the allowance be made for the degree of accuracy which we have decided the method capable of yielding, it will be seen that the discrepancy can be made to disappear almost entirely.

Experiments on the Reductive Power of Pure Yeasts: Means for its Measurement.—M. Nastukoff. Taking the power of the ferment of champagne as 1·00, that of the wines of Portugal is 0·75, of *Saccharomyces pastorianus* 0·50, that of *S. apiculatus* 0·25, and that of the yeast of Brussels beer 0·25.—C. R., cxxi., No. 16.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 205).

On the Gases used.—In all my fundamental experiments I used none but air, oxygen, hydrogen, and coal-gas, stored for at least twenty-four hours in large gasometers over water free from organic matter, and made alkaline with lime or baryta to absorb carbonic anhydride. The gasometer used to hold oxygen was one of Pepys's; it held about 1 cubic metre; it was made of copper, and would stand a pressure of 5 atmospheres. The gasometers used for storing air, hydrogen, or coal-gas were bell-shaped and properly counterpoised; they were built of galvanised sheet-iron; they held about 5 cubic metres, and were placed in the basement of the large laboratory, where the tank of alkaline water was put in winter to keep it from freezing.

All tubes connecting the gasometers to the burner were made of lead; they were long and very flexible, so as to yield easily to all requirements; they were washed successively with ammoniated water, pure water, water acidulated with sulphuric acid, and, lastly, with pure water, taking care to leave their inner surface damp.

It was only by the above means that I succeeded in obtaining air, oxygen, and hydrogen completely free from sodium. I always found illuminating gas free from sodium when taken direct from the main.

On the Air.—I have already explained the methods I adopted for obtaining air free from sodium; I need not repeat them.

On the Oxygen.—The oxygen was prepared by the action of heat on a mixture of chlorate of potassium and red oxide of manganese, calcined and washed. Before letting it into the gasometer filled with alkaline water, it was made to pass through three tubulated bottles, the first containing a concentrated solution of hydrate of potassium, and the other two pumice-stone broken up and soaked in a saturated solution of the same hydroxide. After twenty-four hours rest, it was free from all trace of sodium or potassium compounds.

On the Hydrogen.—I have had great difficulty in getting pure hydrogen,—that is to say, hydrogen burning in pure air with a colourless flame, and showing neither the sodium line nor any trace of a continuous spectrum.

I will begin by confessing that I utterly failed to obtain hydrogen which would burn with a colourless flame so long as I used it as fast as I made it. Therefore hydrogen made by the electrical decomposition of water, acidulated with sulphuric acid, in the presence of pure zinc amalgam to retain the oxygen, did not fulfil this condition. It was absolutely necessary to pass it through pure boiling water, to condense the steam in a metallic refrigerator, and to collect and store it for at least twenty-four hours over pure water. I will say the same for hydrogen prepared from zinc and a 10 per cent solution of sulphuric acid. However pure the metal, acid, and water might be, the resultant hydrogen, when ignited at the end of a platinum tube, free from dust, which had been raised to white-heat and then suddenly cooled, burnt in pure air with a reddish-yellow flame, unless it had been passed through pure boiling water and then stored over pure water. The hydrogen used in all my principal experiments was obtained from zinc specially prepared for these researches. More than 40 kilogrammes of this zinc was used. It was freed from all traces of carbon, arsenic, and other bodies likely to form compounds when in a gaseous state. It was made from pure calamine, and had been re-distilled in bulk with well-calcined oxide of zinc, to remove all traces of carbon, and condensed in a fire-clay retort.*

* The hydrogen used in the hydrogen and air blowpipe was made from pure calamine zinc kept melted for some time, and well stirred up with 5 per cent of its weight of powdered fused litharge. The

I facilitated the production of hydrogen by making the zinc reaction take place in pure boiling water, to which was added, little by little, sulphuric acid mixed with an equal volume of water saturated with sulphate of copper, so as to yield a steady current of gas.

By placing the receiving vessel, sometimes glass but generally lead, in a bath of water kept running to prevent rise in temperature, one can obtain hydrogen free from sulphurous or sulphuric acid. In addition to this, during my first trials, I took care, before passing the hydrogen into the gasometer, to pass it through a large flask filled with pumice-stone, broken into very small pieces and moistened with a solution of caustic potash, and a second large flask filled with small pieces of pumice-stone moistened with an acid solution of sulphate of silver. Whenever the rate of evolution of hydrogen did not exceed 100 litres an hour—and care was taken to keep the glass or lead generator at a low temperature—I was unable to detect the formation of either sulphate or sulphide of potassium or sulphide of silver.

This hydrogen, when received into the gasometer, and tested directly after its preparation, even after passing through pure boiling water, burns with a slightly luminous flame, sometimes slightly yellow, sometimes slightly orange or even reddish; but it is noticeable that, in proportion as it is left over water made alkaline by lime or baryta, so it loses this property until it is entirely deprived of it. Notwithstanding the numerous trials to which I have subjected it, I have not succeeded in determining the nature of the substance which gives hydrogen the property of burning with a slightly reddish flame.* So long as the flame has the least yellowish tint, spectrum analysis shows the sodium D line in it. In order to guard against atmospheric impurities I took the precaution, during my experiments, of effecting the combustion of hydrogen in an inverted bell-jar holding 20 litres, with a neck the edge of which was ground and polished, closed by a flat metal lid, which was also ground and polished, kept at a low temperature by cold running water. The bell-jar, whose surface was damp, was filled with air continually renewed from the top, and freed from sodium by the method mentioned above. A metal tap was screwed into a hole in the centre of the cover, so as to enable me to renew the air conveniently, and the tap was put into direct communication with the domed gasometer filled with purified air. I was thus able to satisfy myself that the colouring of the hydrogen flame was as often due to the surrounding air as to the hydrogen itself, and that this latter case occurs always when one tries to burn the gas as soon as it is made.

In pure air and complete darkness, pure hydrogen—issuing from a clean platinum burner—burns with a flame so devoid of brilliancy, so little luminous, that I was often obliged to put a piece of platinum wire in it in order to see it. The invisibility of the hydrogen flame is furthermore shown by the introduction of oxygen, and even of pure air. Thus when the height of the flame is diminished one-half by the presence of oxygen, the hydrogen becomes incandescent—that is to say, luminous—when burning, and one notices a deep and very pure blue light, always supposing that the air and oxygen supplied are free from sodium. If the hydrogen or the air show traces of so-

alloy of zinc and lead made thus is free from all trace of carbon; with a 10 per cent solution of sulphuric acid it gives off with great ease hydrogen, which, after remaining twenty-four hours in a gasometer in contact with alkaline water free from organic matters, burns in pure air with a colourless flame. Having ascertained that hydrogen set free by the action of zinc and lead on dilute sulphuric acid was, by remaining over alkaline water, entirely deprived of the property of burning with a slightly luminous flame, I henceforth used only hydrogen prepared in this manner in the hydrogen and air blowpipe. But in this case I have always interposed a glass bottle, 12 litres capacity, with two stopcocks filled with small pieces of pumice-stone moistened with a strong solution of caustic potash, and a counterpoised zinc-domed gasometer, 1 cubic metre capacity, charged with baryta water, between the leaden flask with stopcocks, in which the gas was produced, and the burner used to burn it.

* For researches made on this subject, see *NOTES (CHEM. NEWS, vol. lxxii., p. 190).*

dium, the light is a pale and slightly greenish blue. I have already mentioned that as soon as hydrogen is brought to incandescence, platinum melts in it, and spectrum analysis of the flame shows a *continuous* spectrum. On increasing the volume of oxygen, so as to reduce the flame to about four-fifths of its height, the blue colour is not increased—on the contrary, it appears diminished; at the same time the continuous spectrum gains in clearness; one sees indications of the appearance of lines; but in spite of all efforts it was impossible for me to determine their position in a spectrum which, I repeat, was *too strongly luminous*.

I did not succeed in getting hydrogen to burn in an excess of oxygen by the method I employed; every time I supplied oxygen sensibly in excess of half the volume of hydrogen, combustion started in the platinum nozzle and from thence extended to the pipe of the burner itself, which, although of platinum, began to melt. I consider the combustion of hydrogen in a sensible excess of oxygen to be impracticable with the blowpipe used by Mr. G. Matthey, even under a pressure of two atmospheres.

(To be continued).

THE DETERMINATION OF SELENIOS ACID BY POTASSIUM PERMANGANATE.*

By F. A. GOOCH and C. F. CLEMENS.

THE fact that sulphurous and tellurous acids may be oxidised quantitatively by a sufficient excess of potassium permanganate suggests naturally the application of the same general method to the determination of selenious acid. It is the object of this paper to record the results of experiments in this direction.

Brauner (*Journ. Chem. Soc.*, 1891, p. 238) found that in the action of the permanganate upon tellurous acid, whether in a solution acidified with sulphuric acid or made alkaline by caustic soda, the reduction of the permanganate does not proceed to the lowest degree of oxidation, the tellurous acid being unable to reduce the higher hydroxides of manganese which separate. In employing the reaction quantitatively it is necessary, therefore, to add the permanganate in distinct excess, and then to destroy the surplus by means of standard oxalic acid added to the solution acidified with sulphuric acid, subsequently determining the excess of oxalic acid in the warmed solution by addition of more permanganate. The difference between the amount of permanganate actually used and that required to oxidise the known amount of oxalic acid introduced should naturally be the measure of the tellurous acid acted upon. Brauner found, however, an error in the process, by no means inconsiderable, due to the decomposition of the permanganate outside the main reaction. In a subsequent paper from this laboratory (Gooch and Danner, *Amer. Journ. of Science*, xliv., 301) it was shown that if the precaution is taken to restrict the amount of sulphuric acid present in the solution when the permanganate acts, the secondary decomposition involving loss of unutilised oxygen is kept within narrow bounds. In our work upon the oxidation of selenious acid we have followed the suggestions gained in the treatment of tellurous acid by Brauner's method.

The selenium dioxide which we employed was prepared from so-called pure selenium by dissolving the element in strong nitric acid, removing the nitric acid by evaporation, treating the aqueous solution with barium hydroxide to throw out any selenic acid formed in the oxidation, evaporating the solution to dryness, and subliming and re-subliming the residue in a current of dry air until the product was white. The oxide thus prepared was weighed

out for individual experiments or was dissolved in a standard solution from which definite portions were drawn for use.

In the first series of experiments, the results of which are recorded in Table I., the selenium dioxide was dissolved in 100 c.m.³ of water, 10 c.m.³ of sulphuric acid of half strength were added; an approximately decinormal standardised solution of potassium permanganate was added until the characteristic colour predominated over that of the brown hydroxide deposited during the oxidation; oxalic acid in solution of known strength was introduced until the excess of permanganate had been destroyed and the insoluble hydroxide dissolved; and, finally, after heating the solution to about 80° C., more of the permanganate was added to the colour reaction. The final volume varied from 250 c.m.³ to 350 c.m.³, so that the sulphuric acid (absolute) present varied from about 5 per cent at the start to from 1½ to 2 per cent at the end.

When the permanganate is first introduced into the acidified solution the colour vanishes, leaving a clear colourless liquid; but as more is added the solution becomes yellow, and deepens gradually in colour to a reddish-brown, until turbidity, due to the deposition of a brown hydroxide of manganese, ensues, and finally the characteristic colour of the permanganate is plainly distinguishable. The exact point at which precipitation of the manganic hydroxide begins depends upon the dilution, acidity, and temperature of the solution. In experiments (1) and (2) the permanganate was added to the cold solution at the first, but the liquid was heated after the addition of oxalic acid, and before the final titration with the permanganate. The remaining determinations of the series were made in solutions kept hot throughout.

TABLE I.

[Se=79.1, O=16.]

	SeO ₂ taken.	Oxygen equivalent of permanganate used.	Oxygen equivalent to oxalic acid used.	SeO ₂ found.	Error.
	Grm.	Grm.	Grm.	Grm.	Grm.
(1)	0.1000	0.03026	0.01571	0.1010	0.0010+
(2)	0.1002	0.03038	0.01578	0.1014	0.0012+
(3)	0.0997	0.02634	0.01182	0.1008	0.0011+
(4)	0.0999	0.02568	0.01122	0.1004	0.0005+
(5)	0.1000	0.02536	0.01077	0.1012	0.0012+
(6)	0.1000	0.03226	0.01765	0.1015	0.0015+
(7)	0.1001	0.04455	0.02992	0.1016	0.0015+
(8)	0.2001	0.05448	0.02543	0.2018	0.0017+
(9)	0.1997	0.05219	0.02318	0.2014	0.0017+
(10)	0.1997	0.05215	0.02318	0.2011	0.0014+
(11)	0.5178	0.13215	0.05721	0.5203	0.0025+
(12)	0.5197	0.14105	0.06541	0.5252	0.0355+

An examination of these results develops the fact that the action proceeds regularly in the main under the conditions of experimentation, but that there is an apparent waste of permanganate in the process. It was observed that the addition of a little permanganate beyond the exact amount necessary to produce the end-reaction occasioned the precipitation of manganese hydroxide, evidently, according to Guyard's reaction, by interaction between the permanganate and the manganous sulphate present. Plainly the amount of sulphuric acid present, which we kept purposely low to obviate the spontaneous decomposition of the permanganate, was not sufficient to prevent the ultimate formation of the hydroxide at the temperature of action. The natural inference is that the difficulty in the determinations may have been due rather to an interference with the colour reaction at the end of the oxidation process, due to the incipient tendency of the permanganate to act upon the manganous salt, than to direct loss of oxygen from the permanganate. If this is true, the obvious and simple remedy should be found in effecting the oxidation of the oxalic acid at the end of the process at a temperature so low that the inclination

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. 1., July, 1895.

of the permanganate and manganous sulphate to interact shall be diminished. Table II. contains the record of experiments in which this precaution was taken. The entire process of oxidation, which was otherwise similar to that of the previous experiments, was brought about between the temperature of 75° C. at the beginning and 50° C., or even a little less, at the end. The end-reaction was in every case sharp, and the final colour was permanent for several minutes at the least.

TABLE II.

SeO ₂ taken. Grm.	Oxygen equivalent of permanganate used. Grm.	Oxygen equivalent to oxalic acid used. Grm.	SeO ₂ found. Grm.	Error. Grm.
(13) 0.1000	0.03506	0.02065	0.1001	0.0001+
(14) 0.1000	0.03519	0.02073	0.1004	0.0004+
(15) 0.1000	0.03706	0.02255	0.1007	0.0007+
(16) 0.1000	0.03853	0.02422	0.0994	0.0006-
(17) 0.1000	0.03512	0.02065	0.1005	0.0005+
(18) 0.2000	0.06124	0.03256	0.1994	0.0006-
(19) 0.2011	0.06069	0.03177	0.2008	0.0003-
(20) 0.2004	0.06072	0.03177	0.2010	0.0006+
(21) 0.2020	0.06083	0.03185	0.2012	0.0008-
(22) 0.2038	0.06106	0.03185	0.2028	0.0010-

These results are evidently an improvement upon those of the first series of experiments, and are fairly satisfactory so far as concerns the estimation of the amounts of selenium dioxide discussed. The determination of large amounts of selenious acid by this method is somewhat less advantageous than it would be if the reduction of the permanganate proceeded farther in the first action. One hundred c.c. of a standard solution is as much as can be conveniently handled in a single process of titration, and that volume of decinormal permanganate (which is about as strong as the standard solution should be when accurate work is expected) is capable of oxidising about 0.25 grm. of selenium dioxide.

The process which we recommend consists, in brief, in the addition of standard potassium permanganate to the solution of selenious acid containing not more than 5 per cent of its volume of strong sulphuric acid, the introduction of standard oxalic acid until the liquid clears, and the titration of the excess of oxalic acid by permanganate, at a temperature not much exceeding 50° or 60° C. The permanganate and the oxalic acid should be standardised under similar conditions of acidity and temperature, and for a standard of final reference we prefer pure crystallised ammonium oxalate.

We have made experiments in which the initial oxidation of the selenious acid was made in alkaline solution, but inasmuch as the amount of permanganate required for the oxidation is about three times as great as that needed in the acid solution, the treatment in alkaline solution is practically inferior.

THE ESTIMATION OF THE HALOGENS IN MIXED SILVER SALTS.

By F. A. GOOCH and CHARLOTTE FAIRBANKS.

KNOWN methods for the estimation of chlorine, bromine, and iodine in mixed silver salts depend either upon the reduction of the salts to metallic silver or their conversion to a single definite silver salt. The old but by no means ideal methods for the determination of chlorine and bromine in mixed silver chloride and bromide, by reduction of the salts to silver in hydrogen at high temperatures or conversion to silver chloride in an atmosphere

of chlorine, are typical. Perhaps the best of all are the electrolytic method of Kinnicutt (*Am. Chem. Jour.*, iv., 22) for the reduction of the fused chloride and bromide, the battery process of Whitfield (*Am. Chem. Jour.*, viii., 421), which involves the electrolysis of the solution of the silver salts in potassium cyanide, and the method of Maxwell-Lyte (*CHEM. NEWS*, xlix., 3), according to which the silver in the cyanide solution of the silver salts is thrown down by potassium iodide and sulphuric acid. Even in these processes there are points against which objection may be raised with reason. Thus, in the processes of Whitfield and Maxwell-Lyte, it is next to impossible to secure complete and speedy solution of the dried silver salts in potassium cyanide without recourse to intermediate washing and treatment with nitric acid; and in Kinnicutt's method, which has been applied only to the analysis of the mixed chloride and bromide, difficulty is found in the speedy removal of all sulphuric acid from the spongy mass of silver formed in the reduction.

We have tried many experiments with a view to simplifying the analysis of the mixed silver salts. Ignition with mercuric cyanide according to Schmidt's method for sulphides (*Ber. d. Chem. Gesell.*, xxvii., 225); treatment with cuprous chloride dissolved either in ammonia or in hydrochloric acid; the action of ferrous oxalate dissolved in potassium oxalate, Eder's reagent (*Ber. d. Chem. Ges.*, xiii., 500); treatment with chromous chloride or chromous acetate; contact with powdered magnesium under dilute acid; and many other plans of action with powerful reducers have failed to yield analytical results comparable with those of the known methods. Hydrogen sulphide, dry or moist, and ammonium sulphide attack the halogen salts of silver with varying intensity, the chloride very easily, the bromide with less ease, and the iodide most difficultly—as might be predicted from a knowledge of the thermal values involved in the reactions. A current of hydrogen sulphide charged with ammonium sulphide effects the complete conversion of silver chloride to silver sulphide at a temperature below 200° C.; but we have never succeeded in securing absolutely complete conversion of the bromide to the sulphide by similar treatment, even at much higher temperatures, and the iodide resists conversion more obstinately than the bromide. Nor have we been able to find conditions under which the chloride may be converted while the bromide and iodide remain unattacked. In a study of the conditions best adapted to the reduction of silver salts electrolytically, we have obtained results which point to advantageous modifications of the methods heretofore known. We find that the treatment of the fused salts may be simplified, made more accurate, and extended to mixtures containing silver iodide.

In Kinnicutt's process the difficulties lie, first, in the impossibility of destroying the paper upon which the silver salts have been collected and washed, without affecting the reduction of the salts; secondly, in the obstinacy with which the spongy silver holds the sulphuric acid during washing; and thirdly, in the tendency of the chlorine liberated, when a chloride is present, to attack the electrodes.

Upon the first point nothing need be said; the difficulty is obvious and well known. As to the second source of error, our experience shows that rapid washing is not sufficient to remove the sulphuric acid included in the reduced silver, even when excessive amounts of wash-water are used; but that a considerable time is indispensable for the escape of the acid from the silver to the wash-water by diffusion. In several cases we have found errors, ranging from a single milligramme to six or seven, due to inclusion of the acid in residues which had been washed freely but rapidly, and which even after ignition, yielded slowly hot-water extracts, which gave the test for a sulphate by barium chloride.

The results of some experiment made to test the effect of the halogens set free in electrolysis are shown in the accompanying table:—

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. i., July, 1895.

Electrolyte 15 c.m. of H ₂ SO ₄ (15 per cent) with the substance named.	Strength of current in amperes.	Time in hours.	Change in weight of the con- taining crucible.	Change in weight of wire electrode.	Con- nection of crucible.
			Grm.	Grm.	
1.7 grm. KI	0.46-0.25	24	0.0000	0.0000	Cathode
1 " KBr	0.50-0.18	35	0.0000	0.0000	Cathode
1 " KCl	0.48-0.18	26	0.0008-	0.0001-	Cathode
0.5 " HCl	—	—	*0.0009-	0.0000	Cathode
0.5 " HCl	0.3	48	0.0004-	0.0004+	Anode

* Platinum tested for and found in solution.

So it appears that while neither bromine nor iodine attacked the platinum perceptibly under the conditions of the experiments, though set free in abundance, an appreciable amount of the metal did dissolve under the action of chlorine. Moreover, the solubility seems to depend chiefly upon the area of surface exposed, and not upon the electric polarity. The metal dissolved was re-precipitated by the action of the current only in the experiment in which, by reversing the direction of the current, and thus making the area of the anode large while that of the cathode was diminished, a corresponding increase of current density upon the cathode was brought about. It is obvious that, under ordinary conditions of electrolytic reduction, the solvent effect of the chlorine upon the platinum will naturally produce an apparent deficiency in the weight of silver reduced.

These sources of error in the electrolytic reduction of the fused silver salts we have endeavoured to overcome. The danger of change in the constitution of the salts during preparation for weighing we avoid by collecting them upon asbestos in a perforated crucible instead of upon paper; but in order to secure perfect electrical conductivity throughout the mass of silver salts subsequently collected, dried, and weighed, we place a disc of perforated platinum foil upon the prepared felt of asbestos. In this way perfect electrical contact is obtained, though the rapidity of filtration is somewhat impaired. The disc also serves the useful purpose of preventing the disturbance of the felt by the gas evolved from the walls of the crucible in the electrolytic process.* When the silver salts have been collected, washed, dried, and weighed, their fusion is effected by placing the capped crucible upon an anvil and directing the flame of a small blowpipe with care upon the mass from above. The anvil keeps the crucible cool, and tends to prevent the soaking of the asbestos with the fused silver salts, which would be disadvantageous in the washing process which follows the reduction. A rubber band, cut from rubber tubing of suitable diameter, is adjusted so as to cover the junction between the cap and crucible and make a water-tight electrolytic cell. When the electrolytic reduction is finished the band and cap are removed, the crucible is put upon the pump, the liquid is drawn through, and the precipitate washed in the usual manner.

It is obvious that the difficulty of washing out the sulphuric acid from the reduced silver may be avoided if it is possible to substitute for the sulphuric acid an electrolyte which, even if it were not easily removed by washing, should be volatile at gentle heat without affecting the silver; and the danger arising from free chlorine may be obviated by taking care to have the chlorine absorbed by the electrolyte as soon as it is liberated. We find that 25 per cent alcohol containing a tenth of its weight of oxalic acid meets all the conditions for the electrolytic reductions of the mixed chloride and bromide of silver. Such a solution, while possessing sufficient conductivity, absorbs the free chlorine to such an extent that, as we

have found experimentally, no perceptible solvent action takes place upon the platinum, and nothing remains in the silver reduced under such a solution, which is not volatile at gentle heat without affecting the weight of the silver.

In the test-experiments recorded in the accompanying table known amounts of silver chloride and bromide were precipitated, collected, washed, dried at 150° C., and weighed in the filtering crucible, provided as usual with a layer of asbestos, which was in this case covered with the perforated platinum disc. The cap was put in place, the crucible set upon an anvil, and the salts fused with a blowpipe flame in the manner described. The rubber band was adjusted, the crucible nearly filled with the 10 per cent solution of oxalic acid in 25 per cent alcohol, and the current passed in the usual manner, the crucible serving as the negative electrode. When the reduction was judged to be complete the band and cap were removed, the crucible set upon the pump, and filtration of the liquid and washing of the residue carried out as usual. Finally the crucible, cap, and residue were ignited at a very low red-heat and weighed. The entire treatment was repeated until the constant weight of the residue showed that the reduction was complete.

AgCl taken.	AgBr taken.	Ag calculated.	Ag found.	Error.
Grm.	Grm.	Grm.	Grm.	Grm.
1.0608	—	0.7985	0.7990	0.0005+
1.4380	—	1.0823	1.0823	0.0000
0.9998	—	0.7525	0.7525	0.0003-
—	0.9959	0.5721	0.5723	0.0002+
—	0.9979	0.5731	0.5732	0.0001+
1.0044	0.4988	1.0426	1.0422	0.0004-
0.4933	0.4966	0.6559	0.6568	0.0009+

The manipulation of the method is very easy, and the results show that it is capable of yielding accurate results. The current ranged from 0.5 to 0.25 ampère, and for convenience the process was continued over night, though the reduction of amounts such as we treated is usually complete in six or seven hours.

Unfortunately this process, which works so well with the mixture of chloride and bromide, is not applicable to the reduction of silver iodide or to mixtures containing it. Experiment proved that the iodine set free in the electrolysis works over and over again upon the spongy silver, constantly regenerating silver iodide to a greater or less degree. As the result of many attempts to destroy the liberated iodine without introducing anything objectionable into the solution, we finally settled upon a mixture made by neutralising two parts by volume of ordinary (40 per cent) acetic acid with ammonia, adding one part of ammonia, one part of alcohol, and one part of aldehyde (75 per cent). Such a solution we found to work very well on the whole, but as the reduction progresses it frequently happens that a deposit of white ammonium iodate forms upon the anode, which introduces too great resistance to the current. This deposit of iodate is, however, easily removed from the electrode by dipping it into hot water. Whenever the solution is so exhausted that free iodine begins to appear, the liquid should be carefully decanted and replaced by fresh; and before the operation is ended the decanted solutions and the washings of the electrode should be filtered through the crucible and the residue submitted again to the action of the current, to make it certain that loosened particles of silver or silver salt, possibly poured off or removed on the electrode, shall not be lost finally. The necessity of keeping the process under occasional supervision renders it undesirable to continue the action over night. In some cases of prolonged action without attention, we have noticed the formation of gummy carbonaceous matter, which could not be subsequently removed without the application of a degree of heat which might endanger the platinum in contact with the reduced silver. Many of the experiments recorded in the following table were completed within seven hours with a current not exceeding 0.5 ampère.

* This device has been suggested by Puckner (*Journ. Am. Chem. Soc.*, 1893, 710) for holding down the asbestos in an ordinary filtration, and is no doubt of value when suitable asbestos is not at hand. A fairly good asbestos properly prepared, and deposited upon a perforated surface in which the holes are sufficiently numerous—best, as numerous as can be—does not, however, tend to rise during a filtration so long as the suction-dump is in action.—F. A. G.

AgCl taken. Grm.	AgBr taken. Grm.	AgI taken. Grm.	Ag calculated. Grm.	Ag found. Grm.	Error. Grm.
0.4779	—	—	0.3596	0.3591	0.0005 —
0.6096	—	—	0.4588	0.4591	0.0003 +
0.6774	—	—	0.5098	0.5099	0.0001 +
—	0.9969	—	0.5727	0.5726	0.0001 —
—	1.3703	—	0.7872	0.7875	0.0003 +
—	—	1.0613	0.4878	0.4877	0.0001 —
—	—	1.0621	0.4882	0.4875	0.0007 —
—	—	1.0140	0.4661	0.4662	0.0001 +
—	—	1.2012	0.5521	0.5530	0.0009 +
—	—	1.5031	0.6910	0.6914	0.0004 +
0.5035	0.4984	—	0.6653	0.6653	0.0000
1.0020	0.9998	—	1.3285	1.3283	0.0002 —
0.4939	—	0.6561	0.6734	0.6733	0.0001 —
—	0.5000	0.5304	0.5310	0.5316	0.0006 +

These results show that the process affords an accurate reduction of the chloride, bromide, and iodide of silver and mixtures of these salts. When the problem concerns the reduction of the chloride and bromide only, we give the preference to the reduction in alcoholic oxalic acid as being the simpler process. The latter process we have also applied successfully on a larger scale to the recovery of the silver in chloride residues.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, October 25th, 1895.

Mr. WALTER BAILY, Vice-President, in the Chair.

Prof. J. PERRY read a paper by himself and Mr. H. F. HUNT on the "Development of Arbitrary Functions."

During the discussion on Prof. Henrici's paper (April 13th, 1894), one of the authors described a graphical method of developing any arbitrary function in a series of other normal forms than sines and cosines, such as Bessels or zonal spherical harmonics. The method consisted in wrapping the curve which represents the function round a specially-shaped cylinder, not circular, and projecting this curve into a certain plane. Many months were wasted in finding with great exactness a sufficient number of co-ordinates of the trace of the cylinder suitable for a Zeroth Bessel development. The labour, however, was unnecessary, since the co-ordinate most troublesome to calculate is not really needed, the projection only taking place in one direction. To develop any arbitrary function of x (say y) in normal forms, the real difficulty consists in finding the value of an integral, such as—

$$\int_0^a y \cdot Q(x) \cdot dx;$$

where $Q(x)$ is some tabulated function. If now, x is another tabulated function, which is the integral of $Q(x)$, the required integral is—

$$\int y dy.$$

If the values for y for twenty-five equidistant values of x are known, from $x=0$ to $x=a$. Let the corresponding values of x be tabulated, and let a curve be drawn with the values of y as ordinates and the values of x as abscissae; the area between the axis of x and this curve gives the value of the integral required. The authors give four tables containing the abscissae for the four first terms in the development in Zeroth Bessels. They have tested the method by applying it to the calculation of a

known function in terms of zonal spherical harmonics, and the agreement between the true value of the coefficients and those found is very satisfactory.

Prof. HENRICI said the method was a new departure, since in the place of an instrument of complicated design, the authors only used a planimeter and pencil and paper, and obtained the same degree of accuracy. The fact that the series employed to test the method consisted of a finite number of terms seemed to him an objection. Prof. Carl Pearson had, in a recent conversation, informed him of a method for the development of functions which he (Prof. Pearson) had recently discovered. This method was not, however, so simple, at least in most cases, as that of the authors.

Prof. MINCHIN thought it would add to the intelligibility of the paper if it were stated that the method was similar to that employed when expanding in terms of a Fourier series or in spherical harmonics. In these cases you have a function which, when multiplied by other functions of different orders, kills all the terms except one. Graphic methods ought, in his opinion, to be very much oftener employed, and he considered that there was no problem in physical mathematics of which the solution could not be obtained by graphic methods. He would like to know if Prof. Perry had obtained a graphic method of calculating Bessels.

Mr. TROTTER agreed with Prof. Minchin as to the neglect of graphic methods. He regretted that Prof. Perry did not continue to consider the method as the projection from a cylinder, as he had found the method of wrapping curves round a cylinder most useful.

Prof. PERRY, in his reply, said he had adopted the expansion they had employed under the impression that the test was a particularly severe one. He had not discovered a graphic method of calculating Bessels. The reason they gave up the cylinder was the immense labour involved in calculating the y , co-ordinates of the trace, which would afterwards be of no use in the development of the function.

Mr. F. W. LANCHESTER read a paper on "The Radial Cursor: a New Addition to the Slide-rule."

The ordinary form of slide-rule enables calculations to be made which involve multiplication and division; also involution and evolution where the indices are integers. The radial cursor allows of the solution of problems in which fractional indices occur; for example, in questions involving the adiabatic expansion of a gas, where an expression of the form $p v^\gamma = \text{const.}$ has to be dealt with, and where γ is not an integer, nor is it constant for all gases. In this case it is necessary to provide some ready means of dividing the scales on the rule and slider proportionally to the value of γ , which corresponds to the division and multiplication of the respective logarithms of the quantities dealt with in the proportion of the indices of p and v , i.e., x and y . This proportionate division of the scales is effected in the new cursor by a radial index-arm, which is arranged to swing about a stud fixed to a sliding bar running in guides at right-angles to the rule. All readings are taken at the points of intersection of a line on the radius arm and the edges of the slide. The distance of the pivot on which the radius-arm turns from the slide, and therefore the value of the index employed, is read off on a scale fixed to the transverse bar.

Mr. C. V. BOYS said that owing to the kindness of the author he had been able to try the cursor and had found it of great service in dealing with questions of adiabatic expansion. The new addition to the slide rule suffers under the same disadvantage as the rule itself, namely, that a verbal or written description seems so very much more complex than is the actual operation when using the rule. The author's device might be described as an indiarubber slide-rule, for it performed the function of a slide-rule, in which the graduations of the slide were made on indiarubber, so that the ratio of the length of the scale on the rule to the length of the scale on the slide might be

altered at will, and thus involution and evolution with fractional indices performed.

MR. BLAKESLEY asked how powers less than unity were dealt with.

Prof. S. P. THOMPSON and Mr. TROTTER expressed their admiration for the author's method of "stretching" the scale.

Mr. BURSTALL said he had attempted to apply a similar method to the Fuller rule, but did not succeed, since in this rule there was only one scale. He hoped the author's method could be applied in a form such that a greater accuracy than 1 in 300 could be obtained.

Mr. BOURNE thought the fact that the point of intersection of two lines inclined at an acute angle had to be read was likely to limit the accuracy.

The author having replied, the Society adjourned till November 8th.

NOTICES OF BOOKS.

A Laboratory Manual of Organic Chemistry; a Compendium of Laboratory Methods for the Use of Chemists, Physicians, and Pharmacists. By DR. LASSAR-COHN, Professor of Chemistry in the University of Königsberg. Translated, with the Author's sanction, from the Second German Edition by ALEXANDER SMITH, B.Sc., Ph.D., Assistant Professor of General Chemistry in the University of Chicago. Small 8vo, pp. 403. London and New York: Macmillan and Co. 1895.

THE work before us is not one of those manuals of chemistry, organic or inorganic, which during the last few years have become almost painfully numerous. Dr. Alexander Smith is quite justified in saying that it "covers a field not previously occupied," and that it "does not take the place of any of the text-books of organic chemistry, but bears towards them the relation of an almost indispensable complement." It expounds the method used in the laboratory, whether in original research or in verifying results already obtained.

The work consists of two parts, a general and a special. The former treats of baths (for the regulation of temperatures); of crystallisation and dialysis; of decolourising liquids; of distillation, whether ordinary, fractionated, dry, or *in vacuo*; of drying; of extraction; filtration; of the determination of melting-points; of molecular weights; of work in sealed tubes; and of sublimation.

The special methods include condensation, the preparation of diazo-bodies of esters; fusion with caustic alkalis; the preparation of halogen compounds and of nitro-derivatives; oxidation; reduction; the preparation of salts; saponification; the preparation of sulphonic acids; and remarks on ultimate organic analysis. We note the remark that in the case of methylene-di-*p*-toluidine the Kjeldahl method gives the nitrogen 3 per cent too low, whilst the Will-Varentrapp method gives a result in accordance with the theoretical composition.

We think that both teachers and students of organic chemistry will find this book a most satisfactory guide to research.

Quantitative Chemical Analysis. Adapted for Use in the Laboratories of Colleges and Schools. By FRANK CLOWES, D.Sc., F.I.C., Professor of Chemistry in the University College, Nottingham, and J. BERNARD COLEMAN, Assoc. Royal College of Science, Dublin, F.I.C., Head of Chemical Department, South-West London Polytechnic. Third Edition. Post 8vo, pp. 534. London: J. and A. Churchill. 1895.

THE work of Messrs. Clowes and Coleman has evidently given satisfaction to teachers and students, since a third edition is already required. It is admittedly an improve-

ment on its two predecessors, having been again enlarged and enriched with new methods of determination. Additional figures have been introduced for the sake of clearness, and the table of contents has the valuable feature of giving references both to paragraphs and pages.

The bibliography of analytical works will be found of value not merely to students, but even to experienced practitioners.

Part I. treats ably and thoroughly of general and preliminary operations.

Part II. instructs in gravimetric analysis, the various methods being placed in the order of their increasing difficulty.

Part III. treats of the volumetric analysis of liquids.

In Part IV. we find accounts of more complex determinations, both gravimetric, volumetric, and of a mixed character. Here are included the analysis of ores, of important industrial products, waters, foods, and various organic substances.

The simple methods of gas analysis are described in Part V.

The only electrolytic method is that described for the determination of copper.

Upon spectroscopic quantitative analysis the authors do not enter. Methods for the determination of the metals of the so-called rare earths have not been inserted. In the appendix we find what may be called typical results of analyses.

There are also a series of tables of constants for calculating the results of analyses. These, however, seem to us by no means preferable to the tables given in "Rose's Quantitative Analysis," though many of the latter require re-calculating, on account of the more accurate determinations of atomic weights made since 1849.

On the subjects which it includes the work before us is an excellent guide.

The Forces of Nature; a Study of Natural Phenomena. By HERBERT B. HARROP and LOUIS A. WALLIS. Pp. 160. Columbus, Ohio, U.S.A.: Harrop and Wallis. 1895.

THE work before us is a necessarily sketchy survey of the phenomena of the universe, intended, not for the student, general or special, but for the general reader who is desirous of a better acquaintance with the *cosmos* which he inhabits.

In successive chapters, they consider the solar system, the earth, the atmosphere, and sound, chemistry (with the structure of matter), radiant energy, light, heat, and actinism, electricity and magnetism.

The second part consists of what the authors term "disconnected essays and paragraphs on scientific questions," such as the nebular hypothesis, spontaneous combustion, spontaneous generation, argon and helium, and scientific theories in general.

In most instances the authors may be accepted as trustworthy guides; but in speaking of the doctrine of abiogenesis, they overlook the capital part taken in its refutation by the illustrious French philosopher whom the world has just lost. They accept Huxley's prophecy that, in the future, protoplasm will be formed artificially from its lifeless elements. They are believers in the nebular hypothesis and in organic evolution. On the great question of chemistry, whether the elements are absolutely primordial and inconvertible they give no certain sound. They consider the "canals" on the surface of Mars as artificial. The description of snow as rain frozen is much more applicable to hail.

The explanation given of "hypothesis" as a guess having no material foundation cannot be accepted. Most of all must we hesitate at the bold assertion that the simple laws of mechanics govern "the complicated functions of organic life."

We perceive that the authors announce a companion

volume on the "Forces of Life," including the evidences of organic evolution.

Examination of Water for Sanitary and Technic Purposes. By HENRY LEFFMANN, A.M., M.D., Ph.D. Third Edition, Revised and Enlarged. With Illustrations. Philadelphia: P. Blakiston, Son, and Co. 1895.

THE author classifies waters as rain-water, surface-water, subsoil-water, and deep water; the latter being chiefly that obtained from Artesian wells. The instructions concerning taking samples of waters and their analytical examination do not differ essentially from those to be met with in other manuals of the same kind. The instructions for the determination of saline and organic ammonia (known respectively as "free" and "albumenoid" ammonia) are substantially those given by Wanklyn. The Kjeldahl process is described with the remark that it was first successfully applied in water analysis by Drown and Martin. Concerning the Frankland and Armstrong process we read that, "it requires complex and expensive apparatus and special skill, has been shown also to be liable to inaccuracies, and has not come into general use."

For the determination of the nitrogen present as nitrates, the author recommends Hlosway's modification of the Griess process. The oxygen-consuming power of a water may be determined by Tidy's method, modified by Dupré, and for the oxygen existing in solution that of Blarez is proposed.

For the determination of phosphates—a point deemed unessential by many chemists, including Wanklyn—Dr. Leffmann tests with molybdenum solution. We are glad to find that among the poisonous metals chromium is not overlooked—a dangerous impurity which may possibly occur in industrial localities. We can scarcely accept the view that Beggiatoa—commonly called "sewage fungus"—indicates suspended organic matter. It occurs in deep springs charged with sulphur and in sulphuretted industrial waste waters not charged with organic matter.

The author enters to some extent upon the presence, detection, and possible effects of micro-organisms; a subject overlooked in the earlier manuals of water analysis, but upon which biologists and chemists have not yet come to a full and clear agreement.

The work before us is, however, one which the sanitary chemist may with some advantage include in his library of reference.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxi., No. 16, October 14, 1895.

The perpetual Secretary read a letter signed by the Duc de la Broglie, of the French Academy, Leopold Delisle, of the Academy of Inscriptions and Literature, Ch. Harmand, of the Academy of Sciences, Ambroise Thomas, of the Academy of the Fine Arts, and G. Picot, of the Academy of Moral and Political Sciences, inviting the members to be present at a religious ceremony to be celebrated on October 23rd in the Church of St. Germain des Prés in memory of those of the members who have died since the foundation of the Institute. The service will be conducted by the Bishop of Autun.

The President announced the death of Baron Larry, a "free member," which took place on October 8th. Emile Blanchard took occasion to claim for Baron Larry the

honour of having been the advocate of conservative surgery.

Determination of Argon.—Th. Schloessing, jun.—(See p. 211).

Action of Hydrochloric Acid upon Copper.—R. Engel.—The decomposition of hydrochloric acid by copper with the liberation of hydrogen is so slow and so inconspicuous that it has been often overlooked. This acid, in a solution saturated at 15°, is decomposed by copper so rapidly that the liberation of hydrogen may be shown in a lecture. If a little platinum chloride is added to the acid the reaction becomes tumultuous, but soon slackens, so as to be almost imperceptible, though it continues for several years. The decomposition of the hydrochloric acid by copper ceases when the solution contains less than 48.8 to 49 milli-mols. of HCl. Such a solution has a sp. gr. of 1.083 and the composition $\text{HCl} + 10\text{H}_2\text{O}$. The action becomes extremely slow when the liquid is saturated with cuprous chloride. If we pass a current of gaseous hydrochloric acid into water in presence of copper and cuprous chloride the action is rapid. Anhydrous hydrochloric acid is always decomposed by copper.

Action of Potassa and Potassium Ethylate upon Benzoquinone.—Ch. Astruc.—The author has isolated a compound formed by the union of 2 mols. of alcohol and 1 mol. of bipotassic quinone. This derivative is interesting as being formed in presence of an excess of potassa, which seems to indicate that benzoquinone contains only 2 atoms of hydrogen capable of being replaced by potassium.

Combinations of Antipyrin with the Diphenols; Influence of the respective Positions of the Hydroxyls.—G. Patein and E. Dufau.—The diphenols, pyrocatechin, resorcin, and hydroquinone behave in different manners with antipyrin. The ortho- and para-diphenols combine with two mols., but the meta- with one only. The fixation is effected upon one of the atoms of nitrogen by the intervention of phenolic hydroxyl, which loses this property in proportion as its hydrogen is replaced by a metal or a radicle.

Zeitschrift für Anorganische Chemie.
Vol. viii., Part 3.

A Contribution to the Constitution of Inorganic Compounds.—Alfred Werner (Second Communication).—This valuable paper requires the eight accompanying figures. We can merely remark that it is mainly of a controversial character, with especial reference to the recent memoir of Jörgensen on the bases of cobalt, chrome, and rhodium.

A further paper, by the same author, discusses the relation between the co-ordination and valence compounds. It is laid down that the fundamental law regulating the formation of these elements is the effort of the central element to group around itself four radicles.

Atomic Weight of Tungsten.—Mary E. Pennington and E. F. Smith.—The mean value obtained from nine determinations is = 184.921, the maximum result having been 184.943, and the minimum 184.900. The details of the experiments have appeared in the *American Chemical Journal*.

In another paper on the same subject, by E. F. Smith and E. D. Desai, the mean atomic weight of tungsten is given = 184.704.

Specific Heat of Metallic Tungsten.—A. W. Grod-speed and E. F. Smith.—The authors give the value = 6.25, taking the atomic weight of tungsten as 184.921, or = 6.243, on the basis of Smith and Desai's atomic weight.

Double Transposition of Gaseous Bodies.—Henryk Ardowski.—This paper (a translation from the French—or Flemish?) requires the two accompanying figures. The law laid down is an extension of that of

Berthelot—"If the mixture of the vapours of two compound bodies can give on double decomposition a product solid at the prevailing temperature and pressure, whilst the three other products remain gaseous, this will always solidify in a solid form outside of this atmosphere."

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. x., No. 116.

Review of Improvements recently introduced in the Industry of Distillation.—L. Lindet.—This bulky memoir does not admit of useful insertion, the rather as the improvements concerned largely relate to the manufacture of a spirit from beet-root.

Review of the Progress recently effected in the Milling Industry.—M. Colson Blanche.—We are surprised at finding the production of meals and flour classed among the "chemical" industries.

MEETINGS FOR THE WEEK.

MONDAY, 4th.—Royal Institution, 5. General Monthly Meeting. Society of Chemical Industry, 8. "Filtration of Sewage Effluent," by W. J. Dibdin, F.I.C., F.C.S.

WEDNESDAY, 6th.—Society of Public Analysts, 8. "Note on the Bromine and Iodine Absorptions of Linseed Oil," by Rowland Williams. "The Determination of Oxygen in Commercial Copper," by Bertram Blount. "Note on a Recent Milk Case involving an example of Abnormal Milk," and "Note on 'Filled Cheese,'" by R. Bodmer. "The Composition of Condensed Milk," by Messrs. Pearmain and Moor. "Note on the Composition of Commercial Condensed Milk," by A. H. Allen. "Note on the Estimation of minute quantities of Metals in Liquids" and "Note on a Convenient Form of Polarimeter for Examining Essential Oils," by Messrs. Budden and Hardy. "Note on a series of Analyses of a Private Water Supply," by E. Russell Budden.

THURSDAY, 7th.—Chemical, 8. "The Temperatures of Flames and the Acetylene Theory of Luminosity," by Prof. Smithells. "The Action of Acidic Oxides on Salts of Hydroxy-acids," by Prof. G. G. Henderson and D. Prentice. "Sodium Nitrososulphate, and the Constitution of Nitrososulphates," by Profs. Divers and Haga. And other papers.

FRIDAY, 8th.—Physical, 5. "The Magnetic Field of any Cylindrical or Plane Coil," by Mr. Everett. "The Latent Heat of Volatilisation of Benzene," by Mr. Griffiths and Miss Marshall. "The Comparison of Latent Heats of Volatilisation," by Prof. Ramsay and Miss Marshall.

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THE CHEMICAL NEWS.

VOL. LXXII., No. 1876.

BRITISH ASSOCIATION.

IPSWICH MEETING.

SECTIONS A AND B (JOINT MEETING).

Discussion* on ARGON and HELIUM.

THE first item on the agenda was a paper by Lord RAYLEIGH, Sec. R.S., "*On the Refraction and Viscosity of Argon and Helium.*" His lordship stated that what he had to bring forward consisted of little more than certain measurements of the physical properties of these gases. With regard to argon, he might say that the gas he used was prepared from air, at the Royal Institution in London, by what he might call the oxygen method—that was to say, the nitrogen of the ordinary air was removed by the aid of oxygen and with a series of electric sparks. As the proportion of argon in the air, however, was so small—only 1 per cent—the process of separation was extremely slow and tedious. By means of an electric arc, kept up for several weeks in a mixture of oxygen and atmospheric nitrogen, he finally obtained more than 3 litres of argon at atmospheric pressure. Having done this, his primary object was to weigh the gas on the same scale that other gases had been previously weighed, in order to see whether the gas prepared by the oxygen method had the same density as gas prepared by the magnesium method. He might say at once that the density proved to be exactly the same. The other physical properties that remained available for measurement were the refractive index and the viscosity. The refractive index was measured by the interference method. The eyepiece was constructed of cylindrical lenses. To avoid the use of cross-wires, the tubes containing the gases under comparison were arranged so as not to occupy the whole field of view, some light passing parallel to and outside them; two sets of fringes were thus obtained, which could be brought to coincidence by varying the pressure of either gas. Adjustments were made for several pressures, one of the tubes always containing air. The refractive index of argon proved to be 0.961, only about 4 per cent less than that of air.

The next question arose as to the corresponding property of helium. For this purpose he used gas which Professor Ramsay had separated from clèveite, and he was astonished to find that the refractive index of this gas was as low as 0.146. Dry air was in both instances taken as the standard, so that the refraction of helium was about one-seventh part only of that of the air. It might be that at the present time a precisely accurate value of the physical properties of these gases was not of much consequence; but if it should be proved, as was probably the case, that either or both of these gases were mixtures, then a precise knowledge of these properties would be of the utmost importance. The refraction of helium was far below that of any known gas.

The other property that he took up was the viscosity of these gases. By viscosity one meant the force that was called into play when one layer of gas tended to slide upon another; in practice viscosity was usually measured by the rate at which the gas or the liquid could be caused to flow through a very fine capillary tube. There were some difficulties attending this experiment, which he explained, but the results were not very importantly affected. To put the matter shortly, and again taking dry air as the standard, he found that the

viscosity of argon was 1.21, and of helium 0.96. These figures, though less striking than those referring to the refractive index, threw some light nevertheless upon the character of the gases. If they compared oxygen and air, they would find that the ratio was 1.11, oxygen being the most viscous gas previously known; but the figures he had just given showed that argon was more viscous than oxygen, and therefore stood at the head of the list of viscous gases. He hoped that some other members present would point out the chemical conclusions that were to be drawn from these facts.

There was one other point that he should like to mention. Some time last year—in fact almost immediately after Professor Ramsay and himself had established the existence of argon—they obtained, with the assistance of Dr. Arthur Richardson, some gas from the Bath spring which had hitherto been supposed to be nitrogen. At that time he thought that this gas might prove to be in large degree composed of argon. That anticipation was not verified. When the Bath gas was treated in the same way that atmospheric air was treated, in order to isolate what was supposed to be pure nitrogen, it was found that the weight of nitrogen so obtained was not so great as the weight of nitrogen obtained from the atmosphere. The conclusion was that the Bath gas contained less argon than might have been expected; and this rather puzzled him, because argon was more soluble in water than nitrogen. The matter rested for a while, until, in the course of the spring, Dr. Ramsay isolated helium, and found that its density was exceedingly low—only about double that of hydrogen. So far as was yet known, the chemical properties, or want of chemical properties, of argon and helium were about the same, so that any process by which argon was separated, either from air or from the gas of mineral springs, would also separate helium. It was then suggested that the fact which had puzzled them with regard to the Bath gas was explained by the presence of helium, which had obscured by its abnormal lightness the extra density of argon; and he had since ascertained by spectrum analysis that, as a matter of fact, the Bath gas did contain helium. (Applause.)

Dr. J. H. GLADSTONE, F.R.S., who was received with applause, next read a paper on "*Specific Refraction and the Periodic Law, with reference to Argon and other Elements.*" In doing so, he said that in 1869, 1877, and 1883, he had shown that the specific refractive energy of the metallic elements was usually in the inverse order of their combining proportions, and that the specific refractive energies of the elements in general were to a certain extent a periodic function of their atomic weights. The present communication referred to some developments of these old observations. With regard to (1) argon, the specific refractive energy of argon gas, as reckoned from Lord Rayleigh's data, is 0.158. Deeley suggested that this might throw light upon the question whether the atomic weight is 19.94 or double. If the atomic weight be 19.94 the molecular refraction will be 3.15. This figure is almost identical with that belonging to oxygen and nitrogen gas. Taking the specific refractive energy of the elements with atomic weights between 12 and 23, including argon, as 20; viz., carbon 0.417, nitrogen 0.236, oxygen 0.194, fluorine 0.03, argon 0.158, sodium 0.209; argon appears in place on the rise after the great descent from carbon to fluorine. On the other hand, it would seem to be out of place in the neighbourhood of calcium, which has a molecular refraction of 10.0, and a specific refractive energy of 0.248. (2) The fact that the specific refractive energies of the univalent metals are generally inversely as the square root of their atomic weights is confirmed by further research, the product of the two being about 1.3. The same was shown to hold good of the earthy metals in the second column of Mendeléeff's table, the products in that case being fully 1.4. The rule does not apply to the halogens in column VII. As to column VIII., iron, palladium, platinum, and gold all give products

* For portions of this Report we are indebted to the *East Anglian Times*. Proofs have been sent to each speaker for correction.

which are far higher. This confirms the belief that gold is not rightly placed in column I. (3) It is known that the refraction of a salt when dissolved in water is often slightly modified by the proportional amount of the solvent. The author said that he and Mr. Hibbert had recently found that salts of the metallic elements, in columns I. and II. of Mendeléeff's table, showed generally an increased refraction on dilution, those of metals in column VIII. a diminished refraction.

Professor SCHUSTER, F.R.S., then opened a discussion "*On the Evidence to be gathered as to the simple or compound character of a Gas from the Constitution of its Spectrum.*" The purpose they had in introducing this subject, he said, was to inquire whether they could, from the spectrum of a body, draw any conclusions as to the probable nature of the gas, as to whether it was compound or simple, or as to the group of chemical elements to which it belonged. It might appear at first sight that spectroscopists ought by this time to be able to draw some definite conclusions upon these points; but, in order to show the very great difficulties with which they had to contend, he would draw attention to the analogous case—taking the vibrations of sound instead of those of light. If an organ pipe were examined it would be a pretty easy thing to calculate and to learn what different tones that pipe would emit. Supposing, however, that they were outside a room in which bells were placed, possibly half-a-dozen, and that they were asked, simply from the sound of those bells, to conclude how many bells there were, and what was their shape, and the constituents used in making them, then they would be face to face with a problem exceedingly difficult, if not incapable, of solution. It was a difficulty of this kind in which they were placed in regard to the spectrum. He would not go so far as to say that every element behaved differently; but they certainly did not always behave exactly alike, and any conclusions that might at present be drawn from the spectrum of a body must therefore be exceedingly uncertain. Dealing at considerable length with somewhat abstruse facts and theories, the first points presented for consideration were these:—What is it that vibrates in a body which sends out rays and vibrations of light, and how is it possible that bodies which are called monatomic—like mercury vapour, for instance—could show not only a simple vibration of a definite period, but a great multiplicity of lines and a very complicated spectrum? The learned Professor considered that discussion was not likely to be productive of much useful result, simply because they had at present so little knowledge of the facts. His conclusions were that they required in the first place an accurate mapping of the spectra of compound bodies, and some kind of mathematical theory as to the very curious distribution of the wave lengths of both the bands and the lines revealed by the spectrum.

The despondent view of Prof. Schuster was not shared by Prof. RUNGE, of Hanover, who at this point contributed an account of the researches of himself and Prof. Paschen on the spectrum of clèveite gas—undoubtedly the most complete analysis of spectra hitherto made—proving that helium is not a simple element, but consists of two, and not more than two elements. They had proved that the spectrum of clèveite gas consists of two systems, each with three series of lines, six in all; the two systems can be distinguished by the fact that one of them consists of double, the other of single, lines. Prof. Runge described the method of diffusion by which he and Prof. Paschen have altered the relative intensities of the lines in these two systems. They find that the double-line substance, which gives the line D_3 , and ought therefore alone to be called helium, is always present in the sun's chromosphere, and diffuses more slowly than the single-line substance. The latter substance only occurs in spectra of the sun's chromosphere about once in four observations. As he resumed his seat, the young Professor, whose work in this department is well known to those most deeply interested, was loudly cheered.

Lord RAYLEIGH said the audience had already shown their appreciation of the remarkable results that Professor Runge had put before them with such great lucidity, speaking almost as freely as though he had been speaking in his native tongue. (Applause). There could be no doubt that these results were of the highest order of interest. He was not himself an expert in spectroscopic matters; those who were would tell them that there was little work which could be compared in precision and value with that which had now been put before the meeting. The strong evidence given them as to the compound character of the gas from clèveite was a point of the utmost interest. He (Lord Rayleigh) had supposed that the probabilities were not against such a conclusion. The gas was almost of unknown origin; the chemical character of it was unknown, and the manner in which it was held in the mineral was still entirely a matter of speculation. Its division into two elements, and the fact that there were no indications of more than two, seemed to be a point very well made out, so far as one could expect in matters of this kind. He did not know whether Professor Runge could tell them anything of the same sort about argon—whether he had any presumptions from the spectra as to the character of the element or elements it might contain. Without going further, he would leave the consideration of the matter in more competent hands.

Dr. G. JOHNSTONE STONEY, F.R.S., said that his admiration of the splendid piece of work which had been carried on by Prof. Runge and his colleague, dated from the original publication of the results of their investigation some six weeks ago. Then he was so deeply impressed with its importance, in the present position of the investigations with reference to these elements, that he at once wrote to the editors of the *Philosophical Magazine*, and they had inserted a translation (*Phil. Mag.*, Sept., 1895) of the principal memoir for the better information of residents on this side of the German Ocean. Dr. Stoney was just touching upon the paper he had to read, when Prof. Lodge made a private communication to him. Turning aside for the moment, Dr. Stoney said it would be very advisable at that juncture to call attention to the unfortunate position in which scientific investigation in the British Islands stood in comparison with that of at least one other country in Europe. There was no scientific man in these Islands who possessed a laboratory furnished with the appliances for carrying on such investigations as those which had just been placed before the meeting. Their knowledge of the subject was therefore in a somewhat correspondingly backward position. This was a difficulty for which a remedy should, he thought, be found as soon as possible. An apparatus which would measure the half or the third of a tenth metre would really do nothing in an investigation of this kind; they must procure apparatus, like the splendid apparatus in Hanover, which would measure to the fiftieth part of a tenth metre with certainty.

Dr. ARMSTRONG (intervening) said he should like, on behalf of the chemists, who had not said anything up to that time, to express the universal admiration which they must all have of the communications just made to the meeting. He had risen at that juncture not merely with the object of saying this, but also in order to correct the impression which Dr. Johnstone Stoney had just endeavoured to make, at the instigation of Professor Lodge, that they were not capable of doing this kind of work in the British Isles.

Professor LODGE—It was not my instigation. I was just reminding Dr. Stoney of something that I knew, from what he said to me last night, he was anxious not to forget to say. (Laughter).

Dr. ARMSTRONG—And that happens to agree rather curiously with your particular views. (Renewed laughter). The Doctor went on to say that this work had been done in Hanover by individual effort, after the fashion usual in England. If the idea of making such investigations as these occurred to men in this country, who had the

requisite capacity for undertaking them, he was sure that the effort would always be made.

Dr. JOHNSTONE STONEY then read his paper on "*The Interpretation of Linear Spectra.*" The abstract of his argument was as follows:—

In most of the spectra that consist of lines, very remarkable groups present themselves, in which the lines are seen to be associated into definite series. In such cases, except under special circumstances, we may safely presume that all the lines of a group arise from the motion of a single electron in each molecule of the gas. Very striking examples of such groups are present in the absorption-spectrum of oxygen and in the bright line spectrum of carbon. The oxygen of the earth's atmosphere produces the great A group of double lines in the solar spectrum, as well as the very similar great B group, and the a group. It also produces a group more refrangible than D, about which we know less. This group is much fainter than the others, and it is only under exceptional circumstances that it can be seen at all in the solar spectrum. Each of the other three groups can be distinguished into two sub-groups; which from their appearance have been called a head and a train. The general features of these three groups are the same, and Mr. Higgs has made a careful geometrical analysis of one of them, the great B group (*Proceedings of the Royal Society*, March, 1893, p. 200). From his analysis we may infer that the head and the train are due to motions in the molecules which are distinct, although related to one another. This conclusion receives further support from the circumstance, that in the double lines of "the head," it is the violet component of each pair which is the stronger; while in the train it is the red component of each pair which is the stronger. In a paper in the *Scientific Transactions of the Royal Dublin Society* for 1891, p. 563, the present author pointed out that if we proceed on the probable supposition that the motion of each electron is an orbit of some kind going on within the molecules, it can be shown that the partials of the motion of the electron which causes the lines are elliptic partials, and that where an elliptic partial suffers an apsidal perturbation, it divides into two circular sub-partial, giving rise to the two constituents of a double line. We may infer from this that the sub-partial corresponding to the red constituents of the fourteen or more double lines of the train of B are circular motions revolving one way, and that all the violet constituents of these double lines result from circular motions revolving the other way. In order to advance beyond this point, it is necessary to make two further hypotheses which probably are both true. Two hypotheses must here be ventured upon, because observations with the spectroscopic give us no information as to the phases of the elliptic partials or the planes in which they lie. One hypothesis that recommends itself is that the circular sub-partial belonging to a connected series of double lines, e.g., to the train of the great B group, lie in one plane. Another hypothesis which we may venture to make, as a preliminary working hypothesis, is that the amplitude of the motion of the electron has its maximum value at starting, i.e., when that event has occurred at the close of a struggle between two molecules which has set up that motion of the electron which continues during the comparative repose of the quiet, undisturbed journey in which the molecule is indulged after its encounter. With these assumptions it is possible to synthesise all the motions causing the red constituents of the double lines into one motion, which is, however, not circular, but a slowly contracting spiral; and a similar resultant spiral motion turning the opposite way is furnished by the sub-partial forming the violet constituents. While these spirals are being traversed, the radii or semi-amplitudes of the circular motions of which they are composed, and which correspond to the individual lines in the spectrum, are becoming shorter or longer, owing to the escape of energy to the ether or absorption of energy from it; so that the actual orbits are spirals lying somewhat inside or somewhat outside those which

result from the assumption that the radii retain their length. These two spiral motions combine at each instant into a single elliptic motion so elongated that it is nearly a linear vibration, and this elliptic motion continues to represent what occurs, if subjected to the five following perturbations:—

1. A decrease of amplitude.
2. A diminution of periodic time.
3. A slow apsidal motion in a direction opposite to that in which the revolution of the electron in the orbit takes place.
4. A slight fluttering motion which may be represented by a very shallow wave running rapidly round the ellipse.
5. A further slight modification of the form of the ellipse which takes the form of a secular perturbation.

Accordingly we arrive at the conclusion that an elliptic motion undergoing these perturbations is such a motion of an electron as would produce the entire series of lines in the train of B. A similar motion would produce the train of A, of a, and of each of the other similar groups, if such exist in the spectrum of oxygen. These elliptic motions undergoing perturbations may be appropriately called mega-partial in their relation to the actual orbit described in oxygen by the electron that produces all these trains of lines, since that orbit is the resultant which we should get by superposing the motions in these few mega-partial. A similar treatment applied to "the head" of any of the oxygen groups shows that it, too, arises from an elliptic motion subject to perturbations, the chief differences being in the law connecting the falling-off of amplitude and the periodic time, and that the quick fluttering perturbation is absent; also that the apsidal motion takes place in the opposite direction. In oxygen, the strength of the lines of each sub-group fades out towards the red. When the fading is in this direction, it can be shown that the periodic time decreases as the amplitude falls off. Where, as in the carbon groups, the lines fade out towards the violet, the periodic time becomes longer as the amplitude decreases. And, finally, if the lines present themselves, when plotted on a map of oscillation frequencies, as disposed symmetrically on either side of a common centre, this indicates that the periodic time continues unchanged during the shortening of the amplitude. This suggests the cause of the width of spectral lines in general, so far as their width is not merely apparent, i.e., due to the Doppler effect of the translational motions of the molecules, or to the breadth of the slit of the spectroscopic. The rest of the width of the line, as seen, is its true physical width, and seems to be due to the interchange of energy between the molecule and the ether. This leads to diminished amplitude; and this reduction of the amplitude may be accompanied by either a reduction, or an increase, or a persistence unaltered of the periodic time; according to the way in which the motion of the electron is dynamically associated with the rest of the events which go on within the molecule. If the periodic time decreases, this gives rise to a ruling fading out towards the red; if there be an increase of the periodic time, the shading is towards the violet; while if the line fades out both ways symmetrically, there is no change in the periodic time. The relative intensities and the spacings of the lines of the ruling depends on the law which connects the escape of energy, and the shortening of the semi-amplitude; and in its turn this law depends on the dynamical relations in which the parts of the molecule stand to one another. The excessively fine rulings of which the widths of individual lines consist, can probably not be seen otherwise than as a shading, unless perhaps in some very few exceptional instances, owing to their being blurred together by the Doppler effect. We have attributed these very fine rulings to the interchange of energy with the ether. On the other hand, the more conspicuous rulings, such as those we have been studying in oxygen and carbon, seem to be associated with the transference of energy from one motion within the molecule to another. This may be

briefly described by saying that the widths of the individual lines and their being in various ways shaded off, are due to radiation, while that they are arranged in series is due to conduction.

A Discussion followed (the audience having by this time become very thin), the speakers including Professor Liveing, Lord Kelvin, Professor Fitzgerald, and Dr. Macfarlane Gray. Two or three papers on "Orthochromatic Photography" were held over to a later meeting, probably in the Chemistry Section.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 216).

On the Coal-Gas.—When the air is pure, coal-gas taken direct from the main burns in a Bunsen burner, or blowpipe, or blowpipe fed with air or oxygen, without showing a trace of the sodium line on spectroscopic examination. During my examination of the coal-gas spectrum, I tried whether the presence of compounds of ammonia or cyanogen modified it. With this view I examined the spectrum of oxy-coal-gas, made with gas either taken direct from the main or kept in a gasometer where it was stored, having been previously deprived of compounds of ammonia and cyanogen by its passage through flasks filled with broken pumice-stone, and moistened respectively with a strong solution of caustic potash and sulphuric acid diluted with its volume of water. I have never detected any difference between the spectrum shown by ordinary gas and that by the gas purified as above.

With the object of economising oxyhydrogen-gas as much as possible, on account of the difficulty of preparing hydrogen fulfilling all requirements, I often used oxy-coal-gas to eliminate, from compounds, the sodium which is accidentally contained in them. I also used the oxy-coal-gas blowpipe, which is very much easier to manipulate, to check the results given by the oxyhydrogen burner. These requirements led me to examine the oxy-coal-gas jet formed from coal-gas under pressures respectively of *four* and *five* c.m. of water. The results having been the same, I shall limit myself to mentioning here those obtained under constant pressure of *four* c.m. of water.

When the internal surfaces of the service-pipe and burner were thoroughly moistened, the gas-jet issuing from a platinum burner, with a hole 1 m.m. diameter, formed a luminous flame 25 c.m. high and 1½ c.m. diameter. When the supply of oxygen was regulated so that all luminosity disappeared from the flame, its height was reduced to 17 c.m. and its diameter to 7 or 8 m.m.

In pure air this flame is deep pure blue, without an inner cone; spectrum analysis of it shows an absolutely dark spectrum. On gradually increasing the supply of oxygen, the colour intensity of the flame decreases and the light intensity increases; instead of deep blue it becomes sky-blue. It develops at the same time a highly luminous inner cone, pure light blue in the absence of sodium, and pale blue tinged with green whenever it has the least trace of sodium in it. Spectrum analysis of the sky-blue flame and of the inner cone reveals a hydrocarbon spectrum. I found that the luminous intensity was greatest and the spectrum most complete when the inner cone was reduced from its original height of 9 or 10 c.m. to about 5 c.m. Whatever the height of the inner cone might be, the appearance of its spectrum is the same; it consists of six well-marked bands, shaded from left to right: one reddish-brown band, two bands of different shades of green, and three pure blue bands. The bands are defined by lines, the number of which varies with the luminous intensity of the cone. With maximum intensity, examining the apex or one side of the cone, the bands are made up as follows:—

1. The red band—composed of four sharp very bright lines, situated between 43 and 49 on the micrometer of my Steinheil spectroscope. Farther on I shall give its value as a function of Fraunhofer's "A, B, C, D, E, b, F, G, H" lines.*
2. The first green band—composed of four sharp very bright lines, situated between 56 and 66 on the same micrometer.
3. The second green band—composed of three very bright lines, situated between 72 and 77 on the same micrometer.
4. The first blue band—composed of five sharp lines, less bright, situated between 90 and 96 on the micrometer.
5. The second blue band—composed of four faint lines, situated between 113 and 115 on the micrometer.
6. The third blue band—nebulous and very faint, extending from 117 to 118 on the micrometer.

When the luminous intensity was not at its maximum, but yet the bands were broken up into quite distinct lines, the second green band consisted of only two lines and the first blue band of only four lines, instead of three and five lines respectively.

The coal-gas spectrum generally recognised appears then to be an *incomplete* spectrum. The connection between the number of lines in the coal-gas spectrum and its luminous intensity is undoubted, and the influence of a rise of temperature on them both seems to me indisputable.

I made a set of experiments to ascertain what influence the lines in the coal-gas spectrum had on the spectra I was studying under different conditions, and I found out definitely that the spectrum of sodium, potassium, thallium, lithium, calcium, strontium, and barium is the same when rendered incandescent either in an oxyhydrogen or oxy-coal-gas blowpipe. Having obtained the coal-gas spectrum, it suffices to place a compound of sodium, potassium, thallium, lithium, calcium, strontium, or barium in the desired part of the jet, in order to extinguish completely all lines in the coal-gas spectrum, and replace its characteristic bands and lines by the lines of each of these metals.† Doubt is only possible in the case of the green lines shown at a very high temperature by barium compounds. This metal itself has a band made of very fine green lines, as observed by M. Bunsen, that might be mistaken for the green lines in the coal-gas spectrum. I shall be more

* I refrain from giving the exact position of each band and line in the coal-gas spectrum, because in many cases the limit of error in assigning the position is greater than the distance between two adjacent lines.

† I call the appearance of the coal-gas spectrum the *visibility* of the characteristic lines and bands seen during spectrum analysis of the inner cone of an oxy-coal-gas blowpipe, and in the same way I designate by the term *extinction* the non-visibility of lines of bands previously seen. I hold that a spectrum formed of lines and bands can exist in the background of the spectrum without being visible to the sharpest eye. Thus, when one makes, by means of a spectroscopic scale, a spectroscopic examination of a short induction spark without a condenser, between two platinum points, in air free from sodium, and when one refrains from illuminating the spectrum, one always sees a spectrum of atmospheric lines and bands on an absolutely dark background. By then illuminating the spectrum, whether by coal-gas or by the radiation from an incandescent platinum ball, one instantly masks the spectrum of the atmospheric bands and lines; the eye ceases to see them. The bands and lines are in this case replaced by a continuous spectrum, the intensity of which is in proportion, at the same time, to the intensity of the spectrum of the atmospheric lines and to the intensity of the source of light. The observer can at pleasure, and without limit as to the number of repetitions, cause to appear or disappear the two kinds of phenomena. During the revision of my spectroscopic studies with Prof. Depaire, we frequently had occasion to verify the perfect truth of the facts stated above, and we convinced ourselves that it was not possible to obtain by spectrum analysis, even of a short induction spark without a condenser, a spectrum free from atmospheric lines and bands, when we refrained from lighting the micrometer with a luminous scale. The light from the micrometer, whilst extinguishing the spectrum of the atmospheric lines, always replaced it either by diffused light or by a more or less well-defined continuous spectrum. In my opinion it is proved to be impossible to obtain a spark spectrum without atmospheric lines and bands when the background is dark.

explicit on this point when I describe the results of my studies on these last compounds.

The rays from the metallic compounds I have just mentioned extinguish—that is, render invisible—the rays from coal-gas burning in oxygen. The vapours of thallium and sodium, especially thallium, extinguish the lines of coal-gas most easily, but one must raise the vapour of barium compounds to the highest possible temperature before it will make a coal-gas spectrum completely disappear.

Besides this, one finds in some of these bodies this property of extinguishing others. Thus the thallium flame extinguishes barium rays even to the point of masking the spectrum of a spark through barium. I shall return to this subject when describing my studies on the thallium spectrum.

Experience has taught me that, whilst conforming to the conditions mentioned above, I can use indifferently—as I have done—an oxyhydrogen or oxy-coal-gas blow-pipe. In every case I checked my observations the one by the other.

Spectrum analysis of the electric arc passing between *pure* carbon electrodes, and charged with a compound of one of the metals mentioned above, led to results differing from those yielded by spectrum analysis of the oxy-coal-gas blowpipe charged with a compound of the same metals.

However intense the current producing the arc might be, the charging of it by the metallic compounds mentioned did not extinguish the electric carbon lines when they appeared. The spectrum seen showed at the same time, with *perfect clearness*, the characteristic carbon lines and bands, and the characteristic lines and bands of the metallic compound put into the arc. This spectrum showed the lines and bands of both spectra superposed.

When using carbon electrodes for forming the arc I had some work to do to pick out the lines belonging to the carbon spectrum and those belonging to the spectrum of the body put into the arc. I did this sorting with an arc charged with a compound of each of the metals.

In order to be able to make the selection, I first studied the spectrum of carbon in the arc, employing the spectro-scope I had used to examine the *inner cone* of an oxy-coal-gas blowpipe flame brought to its *greatest* luminous intensity; I have given above the results of this latter examination.

When carrying on this delicate work I found, just as M. Fievez has done,* that the *number* and *position* of the lines and bands in an electric spectrum of carbon were identical with the *number* and *position* of the lines and bands in the flame spectrum of oxy-coal-gas.

I found this identity with an arc varying from 4 to 25 m.m. in length, both with the spectro-scope I originally used and with different spectroscopes, as I shall mention later on.

When superposing a coal-gas spectrum on an electric spectrum of carbon, and showing, by this means, the identity of the number and position of the lines and bands in the two spectra, I found that the lines and bands in an electric spectrum of carbon *invariably* stood out on a *continuous* spectrum. This *continuous* spectrum was *entirely wanting* in the appearance of a coal-gas spectrum, whichever spectro-scope might be used.

On account of the presence of a continuous spectrum, more or less intense, according to the luminous intensity of the arc passing between carbon electrodes, when putting into the arc a compound of which one wishes to form an electric spectrum, I have *always* placed the spectro-scope at a suitable distance for diminishing, as far as possible, its intensity, whilst leaving to the lines and bands of the metallic compound sufficient luminosity to permit the identification of the electric carbon lines and bands, which retain sufficient luminosity, varying with

the distance, to allow of a perfectly accurate identification.

One knows, besides, that when using a strong *though short* spark, or an electric discharge in air or hydrogen charged with a metallic compound, it is equally necessary to sort out in the spectrum seen the lines due to the metallic compound, the atmospheric lines and bands, and the hydrogen lines, which are produced at the same time. In my opinion the identification of the carbon bands and lines in the spectrum of an arc made by a current, though very trying to the eye, is easier, on account of the clearness of the lines, than that of the atmospheric bands and lines of the spark and electric discharge, which, however one makes it, always remain more or less diffused, very often masking the sharp definition of lines of the metallic compounds in their neighbourhood.

Notwithstanding all these difficulties, I used, as a *method of checking*, all these different means of producing an electric spectrum of the bodies on which I was carrying on my investigations.

(To be continued).

ON THE ESTIMATION OF SIMPLE CYANIDES IN PRESENCE OF COMPOUND CYANIDES AND CERTAIN OTHER SUBSTANCES.

By J. E. CLENNELL, B.Sc.,
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THE presence of other cyanogen compounds may interfere very seriously with the correct estimation of the simple alkaline cyanide in a given solution. In the treatment of ores by cyanide, various compounds, such as ferrocyanides, sulphocyanides, &c., may be formed.

It is desirable to know the extent to which the presence of such bodies interfere with the estimation of the simple cyanide. A determination of the double cyanides themselves is also useful at times, since it may enable us to judge of the nature and extent of the decomposition of cyanide occurring during the leaching process, and to suggest a suitable means of diminishing this decomposition. It is also sometimes desirable to determine the quantity of the various cyanogen compounds in the solutions leaving the "precipitation-boxes," in order to ascertain the nature of the losses occurring in precipitation, and to decide what means may be adopted for recovering the cyanogen from the compound cyanides contained in these liquors.

1.

The following experiments were therefore made to determine the influence of various substances liable to occur in practice on the estimation of the simple cyanide.

A.—Influence of Ferrocyanides.

The presence of *ferrocyanides* interferes with the correct estimation of the cyanide by means of silver nitrate, causing the indications to be somewhat too high. The error is of importance, however, only when the percentage of cyanide is relatively small. The effect of varying quantities of ferrocyanide of potassium on the estimation of potassium cyanide is shown below. The standard ferrocyanide solution contained 0.5 per cent $K_4FeC_6.3H_2O$.

No. of cyanide test.	Potassium cyanide, 0.1 per cent. C.C.	Potassium ferrocyanide, 0.5 per cent. C.C.	Standard $AgNO_3$ required. C.C.	Strength of KCy indicated. Per cent.	Percentage of error.
1.	25	—	2.5	0.1	—
2.	25	5	2.6	0.104	+4
3.	25	10	2.75	0.11	+10
4.	25	15	2.9	0.116	+16
5.	25	20	2.9	0.116	+16

* "New Researches on the Carbon Spectrum," by Ch. Fievez *Journal of the Royal Academy of Belgium*, 3rd Series, vol. xiv, p. 100.

The error introduced by the presence of ferrocyanide is less when the "iodine" method of titration is used, as shown by the following experiments:—

No. of test.	Potassium cyanide, 0.0954 per cent. C.c.	Potassium ferrocyanide, 0.5 per cent. C.c.	Standard iodine required. C.c.	Strength of KCy indicated. Per cent.	Percentage of error.
1.	25	—	7.45	0.0954	—
2.	25	5	7.50	0.0960	+0.63
3.	25	10	7.45	0.0954	—
4.	25	15	7.60	0.0973	+1.99
5.	25	20	7.55	0.0966	+1.27

B.—Influence of Ferricyanides.

The presence of *ferricyanides* interferes very slightly with the correct estimation of cyanide either by the silver nitrate or by the iodine method. When silver nitrate is used, a reddish brown precipitate of ferricyanide of silver at first appears instead of the white precipitate of cyanide of silver, and re-dissolves as long as an excess of cyanide is present.

A decinormal solution of ferricyanide of potassium was prepared, containing 32.9 grms. per litre.

A mixture was made of 10 c.c. 0.095 per cent potassium cyanide and 10 c.c. N/10 potassium ferricyanide.

This required 9 c.c. standard silver nitrate, indicating 0.9 per cent KCy.

The following tests were made by the iodine method:—

No. of test.	Potassium cyanide, 0.0947 per cent. C.c.	Potassium ferricyanide, 3.29 per cent. C.c.	Standard iodine required. C.c.	Strength of KCy indicated. Per cent.	Percentage of error.
1.	25	—	7.40	0.0947	—
2.	25	5	7.35	0.0941	-0.63
3.	25	10	7.35	0.0941	-0.63
4.	25	15	7.30	0.0934	-1.37
5.	25	20	7.25	0.0928	-2

The amount of cyanide may be estimated with tolerable accuracy by the iodine method in presence of both ferro- and ferricyanide in the same solution.

A mixture was made of 25 c.c. 0.5 per cent ferrocyanide, 10 c.c. 3.29 per cent ferricyanide, and 25 c.c. 0.098 per cent cyanide.

This required 7.3 c.c. standard iodine, indicating 0.1 per cent potassium cyanide, the end-point being quite sharp. The same mixture, tested by silver nitrate, required 3.1 c.c. indicating 0.124 per cent KCy, the end-point being rather indefinite.

C.—Influence of Sulphocyanides.

Sulphocyanate (thiocyanate) of ammonium interferes with the estimation by silver nitrate, rendering the end-point somewhat obscure. It does not appear to interfere with the iodine method.

An approximately decinormal solution of ammonium sulphocyanide was prepared.

(a) 25 c.c. 0.092 per cent KCy and 10 c.c. standard sulphocyanide required 23 c.c. AgNO_3 , indicating 0.092 per cent KCy.

(b) 25 c.c. 0.092 per cent KCy and 25 c.c. standard sulphocyanide required 2.05 c.c. AgNO_3 , indicating 0.082 per cent KCy.

(c) 10 c.c. 0.092 per cent KCy and 10 c.c. standard sulphocyanide required 2.75 c.c. standard iodine, indicating 0.092 per cent KCy. (1 c.c. iodine = 0.00334 grs. KCy).

D.—Influence of Ammonium Carbonate.

It has been pointed out by J. S. McArthur that the indications by the silver method are too high in presence of ammonium carbonate, and that the error may be rectified by the addition of potassium iodide, which forms

iodide of silver, insoluble in ammonium salts. This statement was verified by the following experiments:—

No. of test.	KCy 0.094 per cent. (NH ₄) ₂ CO ₃ .H ₂ O. C.c.	Decinormal AgNO ₃ . C.c.	Standard Percentage of KCy required. indicated. C.c.	Remarks.
1.	25	—	2.35	0.094 Without KI.
2.	25	10	2.45	0.098 " "
3.	25	20	2.55	0.102 " "
4.	25	30	2.60	0.104 " "
5.	25	50	2.65	0.106 " "
6.	25	50	2.40	0.096 With KI.

E.—Influence of Zinc Double Cyanide.

In the presence of the alkaline double cyanides of zinc the indications by both methods are quite indefinite. When any appreciable quantity of zinc is present it is practically impossible to obtain a correct reading. When no other impurity is present the amount of simple cyanide may be arrived at from an estimation—

1. Of the "total cyanide," i.e., the equivalent in potassium cyanide of all the cyanogen present;
2. Of the zinc, from which the amount of double cyanide (e.g., K_2ZnCy_4) may be calculated.

II.

We have now to consider the estimation of the various compound cyanides, in presence of one another, and of the simple cyanides. For practical purposes no method is admissible which is not easily and rapidly executed, and which does not give perfectly definite and unmistakable indications. Many of the methods commonly described in the text-books are therefore excluded.

A.—Estimation of Ferrocyanides.

In the absence of other reducing agents, the estimation of ferrocyanides may be carried out by the method of De Haen, which consists in diluting a measured volume of the solution, acidifying with sulphuric acid, and titrating with potassium permanganate. The presence of *cyanides* and *ferricyanides* does not interfere seriously with this reaction, but it is doubtful whether it would yield reliable results with the impure solutions from the leaching vats and "zinc-boxes." Probably Erlenmeyer's modification, in which the ferrocyanide is first precipitated as Prussian blue, would yield better results, but the estimation would be too tedious for general use.

A standard permanganate solution was prepared, such that—

1 c.c. = 0.04 grm. ferrocyanide ($\text{K}_4\text{FeCy}_6 \cdot 3\text{H}_2\text{O}$).

The following tests were made:—

	(a).	(b).	(c).
0.5 per cent ferrocyanide taken	25 c.c.	50 c.c.	25 c.c.
N/10 ferricyanide taken ..	—	10 "	10 "
0.9 per cent cyanide taken ..	25 "	—	10 "
0.095 per cent cyanide taken ..	—	—	10 "
Permanganate required ..	3.1 "	6.2 "	3.05 "
Ferrocyanide indicated ..	0.496%	0.496%	0.488%

B.—Estimation of Ferricyanides.

The estimation of ferricyanides may be made by Lensen's method, with Mohr's modification.

The presence of *ferrocyanides* does not interfere seriously. In the presence of *cyanides* the indications were found to be somewhat too low.

A decinormal solution of potassium ferricyanide was prepared. (32.9 grms. per litre).

The following tests were made (see Table next column).

C.—Estimation of Zinc Double Cyanides.

An approximate idea of the quantity of zinc in the solution may be obtained by adding a known excess of standard ferrocyanide, and titrating the acidulated solution with permanganate, as in De Haen's method. On

	(a).	(b).	(c).	(d).
N/10 ferricyanide taken, c.c.	10	10	10	10
0.5 per cent ferrocyanide added, c.c.	—	10	—	25
0.9 per cent cyanide added c.c.	—	—	10	—
0.095 per cent cyanide added c.c.	—	—	—	25
Potassium iodide added, grm.	1	1	1	1
Conc. hydrochloric acid added c.c.	2	2	2	2
Zinc sulphate (0.1 per cent Zn) added (neutralised with Na ₂ CO ₃) .. c.c.	10	20	20	20
Number of determinations made	3	2	6	1
Mean N/10 thiosulphate required c.c.	10.03	9.68	9.67	10.05
Ferricyanide indicated, p.c.	3.28	3.27	3.17	3.3

addition of ferrocyanide to the zinc cyanide solution no precipitate is formed at first, but on acidulating the zinc is thrown down as an insoluble ferrocyanide which is unaffected by potassium permanganate. The difference between the amount of ferrocyanide added and the amount found therefore indicates the equivalent of the zinc present. The percentage of zinc found, multiplied by 4, indicates the percentage of potassium cyanide (KCy) which has entered into combination with zinc to form the double cyanide (K₂ZnCy₄).

The following tests were made:—

	(a).	(b).	(c).	(d).
0.9 per cent cyanide taken, c.c.	25	25	25	25
Zinc sulphate solution added c.c.	1	2	3	4
Containing zinc .. grm.	0.01	0.02	0.03	0.04
0.5 per cent ferrocyanide solution added .. c.c.	25	25	50	50
Containing ferrocyanide, grms.	0.125	0.125	0.25	0.25
Permanganate required, c.c.	2.1	1	2.85	1.75
Equivalent to ferrocyanide ..	0.084	0.04	0.114	0.07
Ferrocyanide combined with zinc	0.041	0.085	0.136	0.180
Ferrocyanide per grm. of zinc	4.1	4.25	4.5	4.5

Mean 4.34 grms.

Taking the atomic weight of zinc as 65, and the molecular weight of potassium ferrocyanide (K₄FeCy₆·3H₂O) as 422, then—



The mean of the four tests quoted above showed a proportion of 1 : 4.34.

It therefore appears probable that the following reaction takes place:—



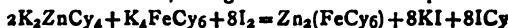
D.—Determination of "Total Cyanide" in presence of Zinc.

If an excess of potassium ferrocyanide be added to a solution containing the zinc double cyanide, and the resulting solution be titrated with standard iodine, a few drops of dilute starch solution being used as indicator, we may determine the equivalent in potassium cyanide of the free alkaline cyanides and the zinc double cyanide. The cyanogen present as ferro- and ferricyanide is, of course, not determined. This method of estimating the "total cyanide" is much simpler and more rapid than the method by precipitation with sodium sulphide previously described (see CHEMICAL NEWS, vol. lxxi., 274), and appears to be equally accurate, provided that other sub-

stances capable of reacting with iodine are absent. Unfortunately, the solutions which pass through the zinc-boxes are subjected to the powerfully reducing action of nascent hydrogen, so that any indications obtained from them by the iodine method are of questionable value. The presence of alkaline sulphides, sulphites, or thio-sulphates would be fatal to the estimation of cyanide by this method.

Solutions containing free hydrocyanic acid must first be neutralised by the addition of caustic soda. Solutions containing free caustic or monocarbonated alkali must first be neutralised by the addition of the necessary quantity of hydrochloric acid (see CHEMICAL NEWS, vol. lxxi., pp. 93, 274).

The following equation affords a simple explanation of the observed result, though several others are possible:—



In any case the cyanogen of the zinc double cyanide is determined as though it existed as free KCy. The zinc ferrocyanide comes down as a dense white precipitate before the end of the reaction, which, however, does not interfere with the observation of the end-point.

With the limitation pointed out above this method yields excellent results.

(a) A mixture was made of 10 c.c. 0.093 per cent KCy and 1 c.c. pure ZnSO₄ (containing 0.001 grm. Zn).

This required from 2.3 to 2.55 c.c. of standard iodine, indicating 0.074 to 0.082 per cent KCy, the end-point being quite indefinite.

The same mixture, to which 5 c.c. of 0.5 per cent ferrocyanide were added, required 2.9 c.c. of standard iodine, the end-reaction being perfectly sharp, indicating 0.093 per cent KCy.

(b) A mixture was made of 10 c.c. 0.25 per cent KCy and 0.5 c.c. pure ZnSO₄ (containing 0.005 grm. Zn).

By direct titration with iodine the indications were quite indefinite, from 0.11 to 0.15 per cent. After adding 10 c.c. of 0.5 per cent ferrocyanide and titrating, 7.65 c.c. iodine were required, indicating 0.245 per cent KCy.

(c) A mixture was made of 40 c.c. 0.25 per cent KCy and 10 c.c. pure ZnSO₄ (containing 0.01 grm. Zn).

10 c.c. of this liquid should therefore contain 0.02 grm. KCy and 0.002 grm. Zn.

The mixture was shaken up with lime and filtered. 10 c.c. of the filtrate were mixed with 1.5 c.c. standard silver nitrate, which gave a strong turbidity, and titrated with N/10 hydrochloric acid, using phenolphthalein as indicator. 1.9 c.c. of acid were required. Another 10 c.c. of the filtrate were mixed with 1.9 c.c. N/10 hydrochloric acid, and 10 c.c. of 0.5 per cent ferrocyanide. This was titrated with standard iodine, 6.15 c.c. of which were required, indicating 0.0197 grm. KCy (by theory, 0.02).

(d) A solution from the "zinc-boxes" was tested as follows:—10 c.c. of solution and 10 c.c. of 0.5 per cent ferrocyanide required 2.5 c.c. standard iodine. 25 c.c. of solution and 10 c.c. of 0.5 per cent ferrocyanide required 6.25 c.c. standard iodine.

Both tests indicating 0.0825 per cent KCy.

Johannesburg, July 5, 1895.

Study of certain Varieties of Graphite.—Henri Moissan.—The author has compared the graphite described in the foregoing paper with the graphite of Ceylon, Borrowdale, Ticondoroga, Greenville, Omesnack (Greenland), Mugrau (Bohemia), Scharzbach, and South Australia. He concludes that the graphites occurring in nature may be classified, as proposed by Sn. Luzzi, as sprouting and non-sprouting varieties. The former seem to have been produced by the action of melted baths, especially metallic baths. The latter may be due to the action of a high temperature on any kind of amorphous carbon.—*Comptes Rendus*, cxxi., No. 17.

SPECIFIC VOLUME AND THE GENESIS OF
THE ELEMENTS.

By C. T. BLANSHARD, M.A.

As I anticipated in a recent article in this journal (CHEM. NEWS, lxxi., p. 285), on "Melting-points of the Elements as a Clue to their Genesis," the question of Atomic and specific volumes provides a further clue. The atomic volumes of certain of the elements will be found to *alternate* in two different ways. It will also be found that the specific volumes, as calculated from observed specific gravities, in certain series of organic compounds, offer striking parallels to various conditions that maintain with the elements.

To take the first case of alternation of atomic volumes of the elements.

If the chemical elements are arranged in numbered series, we find in the eight series represented, that the atomic volumes (with the exceptions of the last three elements in series 2, 6, and 10, and the first two in series 3) alternately rise and fall; *i.e.*, in the odd-numbered series the atomic volumes regularly rise, whilst in the even-numbered series the atomic volumes regularly fall.

1. Hydrogen series.

2.	Li	Be	B	C	N	O	F
At. vol.	11.9	4.9	4.13	3.41	15.6	14.3	—
3.	Na	Mg	Al	Si	P	S	Cl
At. vol.	23.8	13.9	10.4	11.8	14.1	15.4	24.3
4.	K	Ca	Sc	Ti	V	Cr	Mn
At. vol.	44.9	25.6	—	—	9.3	7.45	7.45
" "		Fe	Co	Ni			
		7.1	6.9	6.5			
5.	Cu	Zn	Ga	Ge	As	Se	Br
At. vol.	7.0	9.2	11.8	13.2	15.9	17.6	25.0
6.	Ru	Sr	Y	Zr	Nb	Mo	—
At. vol.	56.4	33.9	—	21.8?	13.3	11.2?	—
" "		Ru	Rh	Pd			
		8.0	8.5	8.8			
7.	Ag	Cd	In	Sn	Sb	Te	I
At. vol.	10.2	13.1	15.3	16.2	17.9	19.5	25.6
8.	Cs	Ba	La	Ce	Nd	Pr	—
At. vol.	70.7	36.5	22.6	21.1	—	—	—
9.	Sa	—	Gd	Tb	—	Er	—
10.	Dp	Yb	—	—	Ta	W	—
At. vol.	—	—	—	—	17.6	9.8	—
" "		Os	Ir	Pt			
		8.5	9.0	9.1			
11.	Au	Hg	Tl	Pb	Bi	—	—
At. vol.	10.2	14.7	17.2	18.2	21.4	—	—
12.	—	—	—	Th	—	U	—
At. vol.	—	—	—	21.1	—	12.8	—

Series 9 should prove to possess rising atomic volumes; that is to say, as the atomic weight increases there will be less and less corresponding increase in specific gravity. The figures for the atomic volumes are those calculated for a table given in CHEM. NEWS, vol. lxx., p. 271, except that more recent values of barium (Ba = 137.43) and cadmium (Cd = 112.06) are taken.

The second way of showing the alternation of atomic volume is by comparing the elements in their natural groups and noting the *differences* between the atomic volumes, as Bazaroff has done in the case of atomic weights. It will be seen that—

1. The differences between the atomic volumes of elements, taken in natural groups, alternate in groups I. and II., and probably also in III. and IV.

2. In V. and VI. the differences increase with the increase in atomic weight.

3. In group VII. the differences are constant.
4. In all the *a* and in all the *b* groups the differences become less with increase in atomic weight.

Group.	Element.	At. vol.	Diff.
I.	Li	11.9	
	Na	23.8	11.9
	K	44.9	21.1
	Rb	56.4	11.5
	Cs	70.7	14.3
II.	Be	4.9	
	Mg	13.9	9.0
	Ca	25.6	11.7
	Sr	33.9	8.3
	Ba	36.6	12.7
III.) IV.)	Data too defective.		
V.	N	15.6	
	P (red)	14.1	-1.5
	As (am.)	15.9	+1.8
	Sb	17.9	2.0
	Bi	21.4	3.5
VI.	O	14.3	
	S (rhomb.)	15.45	1.15
	Se (cryst.)	17.57	2.12
	Te (cryst.)	19.99	2.42
VII.	F	—	—
	Cl	24.3	—
	Br	25.0	0.7
	I	25.6	0.6
I.a.	Cu	7.0	
	Ag	10.25	3.25
	Au	10.20	-0.05
II.a.	Zn	9.2	
	Cd	13.1	3.9
	Hg	14.7	1.6
III.a.	Ga	11.8	
	In	15.3	3.5
	Tl	17.2	1.9
IV.a.	Ge	13.2	
	Sn	16.2	3.0
	Pb	18.2	2.0

Group.	Element.	At. vol.	Diff.
V.a.	V	9.31	
	Nb	13.3	3.99
VI.a.	Cr	7.45	
	Mo	11.17?	3.72
	U	12.79	1.52
VII.a.	Mn	7.45	
II.b.	Fe	7.1	
	Ru	8.05	0.95
	Os	8.50	0.45
IV.b.	Co	6.89	
	Rh	8.50	1.61
	Ir	8.97	0.47
VI.b.	Ni	6.53	
	Pd	8.77	2.24
	Pt	9.06	0.29

The *c* groups do not supply any data, as, being Preyer's series 10 and 11, at most each *c* group contains two elements. But it may be noted, in confirmation of Prof. Preyer's classification, which places Tantalum in what I term group V.c, instead of with Vanadium and Niobium in V.a; that the atomic volume of Ta, 17.6, shows a difference of 4.3 from that of Nb; whereas, by the above laws of differences of atomic volumes, were Ta the third member of the group V.a, it would show a difference of considerably less than 3.99, namely, a difference of about 1.6. The *b* groups in the above classification are Mendeleeff's group, VIII.

The *a* groups may be aptly termed the *copper*, and *b* the *iron groups*. With regard to the differences in atomic volume, it may be further noted that—

5. In the ordinary groups the first differences are low, succeeded by higher ones.

6. In the copper and iron groups (or *a* and *b* groups) the first differences are high, succeeded by lower ones.

(To be continued).

ON THE VAPOUR-TENSIONS OF MIXTURES OF VOLATILE LIQUIDS.*

B. C. E. LINEBARGER.

(Continued from p. 214).

The fourth class of mixtures, of which the only representative here is the mixture of nitrobenzene and carbon tetrachloride, does not, in reality, belong to our subject of investigation, which is to study mixtures of volatile liquids only, and not those of a volatile with an almost involatile one. Still it was thought advisable to find out what the partial tensions of mixtures of such liquids would be, inasmuch as Raoult (*loc. cit.*) has made an elaborate study of the total vapour-tension of mixtures of ether and several almost non-volatile liquids. As is seen in the curve, the partial pressure of the carbon tetrachloride and the total pressure of the mixture are almost identical, just as would naturally be expected. The

curves are, if we regard the right hand ordinate first, at the beginning parallel with the straight line connecting the points representing the vapour-tensions of the pure liquids; they then turn upwards, reach a maximum distance from the straight line at about the abscissæ value of fifty, and then gradually turn downwards towards the origin. I was curious to see if this behaviour was characteristic of the mixtures of liquids investigated by Raoult.

Accordingly I have re-calculated his data so as to get them into a form comparable with mine. These re-calculated data are given in the following small Tables:—

TABLE A.—Vapour-Tensions of Solutions of Turpentine in Ether at 16.2°.

Vapour-tension of Turpentine at 16.2° is 4 m.m. of Mercury.

Vapour-tension of Ether at 16.2° is 377 m.m. of Mercury.

Mols. of Turpentine in 100 mols. of solution.	Vapour-tension in m.m. of Mercury.
5.9	354
12.1	332
23.4	294
35.5	255
47.9	212
64.5	159

TABLE B.—Vapour-Tension of Solutions of Nitrobenzene in Ether at 16.0°.

Vapour-tension of Nitrobenzene at 16.0° is 4 m.m. of Mercury.

Vapour-tension of Ether at 16.0° is 374 m.m. of Mercury.

Mols. of Nitrobenzene in 100 mols. of solution.	Vapour-tension in m.m. of Mercury.
6.0	353
17.9	321
35.5	278
56.2	232
75.9	166
84.0	132

TABLE C.—Vapour-Tensions of Solutions of Aniline in Ether at 15.3°.

Vapour-tension of Aniline at 15.3° is 4 m.m. of Mercury.

Vapour-tension of Ether at 15.3° is 364 m.m. of Mercury.

Mols. of Aniline in 100 mols. of solution.	Vapour-tension in m.m. of Mercury.
3.8	349
7.7	335
14.8	308
20.5	292
49.6	210
68.7	147

TABLE D.—Vapour-Tension of Solutions of Methyl Salicylate in Ether at 14.2°.

Vapour-tension of Methyl Salicylate at 14.2° is 4 m.m. of Mercury.

Vapour-tension of Ether at 14.2° is 306 m.m. of Mercury.

Mols. of Methyl Salicylate in 100 mols. of solution.	Vapour-tension in m.m. of Mercury.
1.1	344.6
2.1	343.6
4.8	332.0
9.2	316.0
15.1	301.0
23.2	281
49.0	208
77.0	125
85.0	101

* Abridged from the *Journal of the American Chemical Society*, vol. xvii., No. 8, August, 1895.

TABLE E.—Vapour-Tensions of Solutions of Ethyl Benzoate in Ether at 11.7°.

Vapour-tension of Ethyl Benzoate at 11.7° is 3 m.m. of Mercury.

Vapour-tension of Ether at 11.7° is 313 m.m. of Mercury.

Mols. of Ethyl Benzoate in 100 mols. of solution.	Vapour-tension in m.m. of Mercury.
4.9	296
9.6	286
27.1	235
53.0	167
75.5	94
94.4	39

If these results be plotted in a system of co-ordinates, the curves will be found to have a close resemblance to the one which I have found for the mixture of nitrobenzene and carbon tetrachloride. It seems likely that this form of curve is the general one for the total tension of mixtures of a volatile with an almost fixed liquid.

(To be continued).

NOTICES OF BOOKS.

The Scientific Foundations of Analytical Chemistry treated in an Elementary Manner. By WILHELM OSTWALD, Ph.D., Professor of Chemistry in the University of Leipzig. Translated, with the Author's sanction, by GEORGE MCGOWAN, Ph.D. 8vo., pp. 208. London and New York: Macmillan and Co. 1895.

PROFESSOR OSTWALD'S work here before us is clearly distinct from the other analytical manuals, large or small, with which we have come in contact. It is concerned not with technical details, but with fundamental principles. Hence, whilst it would not be consulted with reference to the best method of analysing a complex phosphate or titaniferous iron, or a cobalt ore, it may, and should be, considered not merely by the student, but by the experienced practitioner.

We are here reminded that no substance is absolutely insoluble, and that none of our methods of separation and determination are perfect. Suggestions are thrown out which deserve notice. Thus, when speaking of the separation of solids from each other, the author mentions that mixtures of different substances in powder are electrified on shaking, one constituent becoming positive and the other negative. If the mixture is thrown upon an electrified non-conductor, the oppositely charged particles are attracted to it and the others repelled. Again, in a non-homogeneous electrical field the substances with the higher dielectric constants are driven to those spots where the intensity of the field is greatest. No analytical application of this fact has yet been made.

In speaking of the treatment of precipitates, attention is called to the phenomena of adsorption—not to be confounded with absorption.

In the separation of gases from each other we are reminded that not all possible methods have been tried in analysis.

The theory of removing a dissolved substance from the solvent by shaking it up with another is clearly expounded. It is shown that with a given quantity of solvent a more perfect separation is effected if the shaking up is done with many small successive portions rather than with a few large ones.

Concerning heterogeneous equilibrium, the law is laid down that—"In two contiguous spaces or phases the concentration of each substance present in both spaces must bear a constant ratio."

It is admitted that the attempts made to determine the amount of a precipitate without washing it, from the mean specific gravity of precipitate plus liquid and the

specific gravity of liquid alone, have led to no satisfactory results.

The second part of the book shows the application of the principles already laid down. Professor Ostwald repeats that "students who read this book will do so, not so much with the object of learning analytical chemistry from it, as of pondering over the scientific principles which underlie what they have already been taught by actual practice, so as to be able to apply this knowledge with greater freedom and certainty."

We can only hope that many students will thus ponder over these principles.

We regret to find that Dr. McGowan uses as an abridgement for "cubic centimetre," not the simple and unmistakable c.c., as used in France and hitherto in Britain, but the more prolix German expression c.cm.

Report of the Trinidad Government Analyst. Minute (No. 63) from the Acting Governor, accompanying the Annual Report of the Government Analyst for 1894. Trinidad: Government Printing Office, Port-of-Spain.

THE total number of samples examined during the year was 653, of which 626 were official samples. The official samples were sent in by the police in connection with cases before the Courts of Justice, from the sanitary police (food and drugs), the Customs, the Board of Health, the receiver-general, the surgeon-general, and Public Works. Of the official samples 78 were connected with charges of murder, wounding, and indecent assaults; and 69 were cases of suspected poisoning. In 38 of these samples poisons were detected, namely arsenic, mercuric chloride, potassium cyanide, creosote, and preparations of opium. None of the insufficiently known poisonous products of tropical countries seem to have been used.

The adulteration of milk still requires constant vigilance, as 36 per cent of the total samples had been let down with water in the proportion of 25 per cent. Oleomargarine is sold at the same price as butter.

We regret to find that the Colony is adopting the recent error of the home-kingdoms in requiring an addition of mineral oils to methylated spirits. Why not, as is done in Germany, make the methylated spirit undrinkable by the addition of a trace of Dippel's animal oil?

The question of a regular bacteriological examination of water supplied to Port-of-Spain is still under consideration.

Some samples of water from wells in Tacarigua district were found to be worse than many sewage effluents.

Agricultural Journal. Published by the Department of Agriculture of the Cape Colony. Vol. viii., No. 17.

ATTENTION is emphatically called to the value of the sunflower to farmers. It is found to bear the intense heat of central Australia better than any other crop. The seed is an excellent food for poultry. An acre of land yields 50 bushels of seed, from which 50 gallons of oil may be obtained. The oil is excellent for lubricating, and for the manufacture of superior toilet soap, as well as for a clean-burning lamp-oil. The cake left after the expression of the oil is a good cattle-food, being considered in Eastern Europe as the best available cattle-food, superior to rape or hemp cake: 1000 lbs. of dried stalks have been found to yield 57 lbs. of ash, chiefly potash. Hence the stalks and leaves should always be ploughed into the soil.

Particular attention is called to the war against the scale-insects (*Coccidæ*), which have already destroyed the orange and lemon plantations of South Africa. For dealing with these pests an emulsion of paraffin is recommended. A favourite formula is—

Paraffin..	..	..	2 gallons.
Soap ..	..	..	½ lb.
Water ..	..	..	1 gallon.

The water is heated to boiling, the soap stirred in until dissolved; when the mixture is just below a boiling heat the paraffin is stirred in with violent agitation for ten minutes.

Determination of the Atomic Weight of Cobalt. An Inaugural Dissertation presented to the Philosophical Faculty of the University of Basle for obtaining the Degree of Ph.D. By HERMANN THIELE. Submitted December 15th, 1894. Basle: Kreis Printing Works. 1895.

THE author, in criticising the researches of Remmler (*Zeitsch. f. Anorg. Chemie*, ii., p. 221), points it out as a singular fact that the atomic weight of the several fractions operated on by the latter does not rise or fall progressively, but fluctuates up and down. Remmler explains this fact by the presence in the fractions of different quantities of an unknown element, as admitted by Krüss. Hence the investigation had even a greater importance than might have been supposed at first sight, though Dr. Thiele did not find it useful to fractionate the specimens employed in most of his experiments.

He used three methods:—1, weighing cobaltous oxide and the metal; 2, cobaltous chloride and the metal; and 3, weighing the metal and silver chloride. The three determinations made by the first method give an average atomic weight = 58.849. By the second method, six determinations show an average = 58.64; and by the third method, four determinations gave a mean value of 58.801, or, with a correction for the solubility of AgCl in water, 58.770. All the results are calculated for

O = 15.96, Cl = 35.37, and Ag = 107.66.

The author's researches point to a probable value:—Co = 58.765. This result is compared with the most trustworthy recent determinations, i.e., those of Russell 58.59, Lee 58.97, Zimmermann 58.74, and Winkler 59.67. Hence it is pointed out that the author's result agrees exceedingly well with that of Zimmermann, whilst the values of Russell and Lee diverge equally far on each side. Dr. Thiele's results cannot be at all reconciled with that of Winkler. It is stated in a final note that this dissertation was handed in to the Philosophical Faculty of Basle on December 15th, 1894. Hence no reference could be made in it to the subsequent investigations of Winkler (*Zeitsch. f. Anorg. Chemie*, viii., p. 291).

Incidentally it is remarked that we can depend but little upon weights, originally extremely accurate, if they have been used for some time, however carefully.

A careful examination of this pamphlet will convince the reader that Dr. Thiele has used every precaution. His weights (made by Verbeck, of Dresden) displayed, as far as those below 10 grms. are concerned, only in two cases an error of 0.02 m.grm. The weights above 10 grms. were used only for counterpoises, so that their absolute accuracy does not come in question. The balance was made by Bekel, of Hamburg, and had been carefully tested as regards the constancy of its zero-point. The vessels employed were of platinum, or, where this material was impracticable, of Meissen porcelain, or of the so-called "resistance glass" of Koehler and Martini.

Transactions of the Wagner Free Institute of Science of Philadelphia. Vol. iii., Part 3, March, 1895. Philadelphia: Wagner Free Institute of Science.

THE issue before us is entirely devoted to geology and palæontology, and consequently contains no matter which rightfully falls within our purview.

The Free Institute has a faculty comprising departments of chemistry, botany and forestry, geology, physics and astronomy, literature and history, and engineering. Biology seems to have been overlooked. If we might so far presume we would suggest that a biological department should be established, and literature and history

eliminated. We throw out this hint because we observe that in the so-called "literary and philosophical societies" of England, literature monopolises the lion's share of attention, and finds a space in the *Transactions*.

Practical Proofs of Chemical Laws. A Course of Experiments upon the Combining Proportions of the Chemical Elements. By VAUGHAN CORNISH, M.Sc., Associate of the Owens College, Manchester. London and New York: Longmans, Green, and Co. 1895. Pp. 92.

If the multitude of works destined to throw a guiding light upon the course of the chemical student has any prophetic meaning, we ought soon to have a most luxuriant harvest of discoverers and discoveries. Mr. Cornish admits, in his Preface, that the "experimental proofs" might more properly be called "verifications." Without doubt they constitute a useful series of exercises for students who are already acquainted with the qualitative composition of the substances employed, and as such the book deserves recommendation.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxi., No. 17, October 21, 1895.

The Secretary announced the death of Dr. Hellriegel, a correspondent of the Section of Rural Economy, who died on September 24th last at Bernburg (Anhalt). M. Berthelot added that the deceased is distinguished for his beautiful researches on the fixation of nitrogen by leguminous plants, a phenomenon which he successfully traced to the action of bacteria inhabiting certain nodosities on the roots of the vegetables.

Study of a Graphite Extracted from a Pegmatite.—Henri Moissan.—This paper will be inserted in full.

Study of the Latent Heats of Evaporation of the Acetones of the Fatty Series, Octane, Decane, and of the Two Ethers of Carbonic Acid.—W. Louguinine.—From his experiments the author concludes that for each of the groups which have been studied the volume of MS

T is approximately constant. In this expression M represents the molecular weight of the substance, S its latent heat of evaporation, and T its absolute temperature of ebullition. For different groups of substances it varies in a decided manner (from 26.5 to 19.8).

Potassic Peroxidic Derivatives of Benzoquinone.—Ch. Astré.—The author's results show the diketonic nature of benzoquinone.

Composition of the Rices Imported into France.—M. Balland.—Rice is a more nutritive aliment than is commonly supposed, and it would be advantageous to restrict the use of glazed rices, and to favour the consumption of the natural grain simply deprived of its husk.

Toxicity of Acetylene.—M. Gréhant.—The author infers from his experiments that acetylene is poisonous if inhaled in large quantities. This gas can be easily detected in the blood by means of the "grisometer." It is, however, much less poisonous than coal-gas. Its mixtures with oxygen are highly explosive.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xiii.-xiv., No. 14, 1895.

Action of Nitrogen Peroxide upon the Haloid Salts of Antimony.—V. Thomas.—On dissolving a

haloid antimony salt either in chloroform or in carbon disulphide, and passing into the solution a current of nitric oxide, we generally obtain a white crystalline precipitate, which, however, ceases to form after a certain time. The author thought that it might be due to traces of nitrous vapour. He took a stoppered flask, from which the air had been carefully expelled by a current of carbonic acid, and containing a chloroformic solution of antimony trichloride. Into this was passed a current of dry nitrous oxide, perfectly free from peroxide. No precipitate was formed until the flask was unstopped, when it was immediately formed. The precipitate had the composition $\text{Sb}_4\text{O}_{11}\text{N}_2\text{Cl}_4$. With tribromide dissolved in chloroform the result is analogous, but the precipitate contains no bromine, and has the composition $\text{Sb}_4\text{O}_{11}\text{N}_2$.

Molecular Modifications of Glucose.—C. Tanret.—The author calls the ordinary glucose α , that which when crystallised gives the highest rotatory-power $\alpha_D = +106^\circ$; glucose β is the modification of a constant rotatory-power $\alpha_D = +52.5^\circ$; and glucose γ is that which gives at once the lowest rotatory-power $\alpha_D = +22.50^\circ$.

New Synthesis of Some Aromatic Nitriles.—A. Desprez.—The author has supposed that cyanogen, like chlorine, might be substituted for hydrogen in organic compounds. He applied the process for the present to five carbides, which he succeeded in transforming into nitriles, namely, benzene, toluene, two xylenes, and mesitylene.

Causes of the Colouration and Coagulation of Milk by Heat. Formation of Formic Acid at the Expense of Lactose.—P. Cazeneuve and E. Haddon.—Already noticed.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. x., No. 116.

Combustion of Mineral Oils in Common Lamps.—P. Kouindji.—This paper cannot be reproduced without the four accompanying figures.

Matches with Explosive Pastes.—Th. Schloesing.—The entire replacement of phosphorus in the manufacture of matches does not seem to be as yet very near. Even the substitution of explosive pastes for those with white phosphorus is not so simple a matter as it might seem at first sight.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on November 4th, Sir James Crichton-Browne presiding. The following were elected Members:—H.R.H. Prince Louis Philippe, Duc d'Orleans, Sir John Evans, K.C.B., F.R.S., The Hon. Adrian Verney Verney Cave, Mr. Walter Allcroft, and Mr. James Beale. The Managers reported that the late Mr. John Bell Sedgwick, M.R.I., had bequeathed £300 to the Royal Institution in aid of the Fund for the Promotion of Experimental Research at Low Temperatures. The special thanks of the Members were returned to Sir Frederick Abel, Bart., for his donation of £50 to the Fund for the Promotion of Experimental Research at Low Temperatures.

Conversazione at the Melbourne College of Pharmacy.—This very successful demonstration comprehended an exhibition of specimens and appliances bearing on pharmacy, such as plants of medicinal and technical interest, polariscopes and micro-spectroscopes (both instruments which ought to be more familiar to the pharmacist than they generally are), collections of useful and destructive insects, bacteriological specimens, fluorescent liquids, &c. As an instance of utter irrelevance there figured a "philatelic" collection. A short lecture was given by Dr. F. Howell Cole on "Toxins and Antitoxins," and one by Mr. Plowman on "The Romance of Cocaine." A

prolonged investigation on a case of arsenical poisoning did not involve any analytical question. In a prosecution at Adelaide, under the Food and Drugs Act, the question was raised "What is vinegar?" The City Analyst held that vinegar for dietetic use should be composed of alcohol, mucilage, extractive matter, acetic acid, and acetic ether. The University Analyst maintained that the term vinegar was a generic one, and should mean a naturally fermented vegetable infusion. Mr. Scammell declared that pure acetic acid and water was vinegar, and that fermentation was not necessary. — *The Pharmaceutical Journal of Australasia.*

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THE CHEMICAL NEWS.

VOL. LXXII., No. 1877.

NOTE ON THE FORMATION OF CITRIC ACID BY THE OXIDATION OF CANE-SUGAR.

By ALFRED B. SEARLE and ARNOLD R. TANKARD.

SINCE the publication of Dr. Phipson's third note on the formation of citric acid by the oxidation of cane-sugar, we have continued our experiments on this subject, and have attempted to obtain citric acid by a strict adherence to the conditions last prescribed by Dr. Phipson (CHEM. NEWS, vol. lxxii., p. 190).

Equal weights of cane-sugar, concentrated nitric acid (sp. gr. 1.42), and potassium permanganate were taken, the last-named reagent being added in the form of a strong aqueous solution. The liquid became as clear as water in about half an hour after the last addition of permanganate. This solution was then allowed to stand for twenty-four hours, and at the end of that time was neutralised by the cautious addition of chalk, the liquid being frequently agitated. When the liquid ceased to have an acid reaction to litmus, it was filtered and the filtrate boiled for some minutes. No precipitate was produced even after the addition of a strong solution of calcium chloride and further boiling, thus showing the absence of any notable quantity of citrate.

The matter on the filter dissolved with effervescence in acetic acid, showing that an excess of calcium carbonate had been used. We fail to see how Dr. Phipson avoided the use of an excess of calcium carbonate in neutralising the acid solution.

We have also used sulphuric acid in place of nitric acid, acidulating the cane-sugar solution. In this case, the clear solution, after standing in the cold for twenty-four hours, was neutralised by the addition of chalk, and filtered. This filtrate, on boiling for some time, deposited a white crystalline precipitate, which was filtered off and washed with hot water. It was then dried at 100° C., and subjected to such tests as were described in our previous paper (CHEMICAL NEWS, vol. lxxii., p. 31).

The results in every respect confirmed those formerly obtained, and showed the substance to be composed entirely of hydrated calcium sulphate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

Dr. Phipson, in his third note (CHEMICAL NEWS, vol. lxxii., p. 190), states that it is easy to point out where our error lies, but that it will perhaps not be so easy to get us to acknowledge it. We do not deny that citric acid may be formed by the oxidation of cane-sugar under suitable conditions, but we do assert that the mode of operating prescribed by Dr. Phipson fails to produce citric acid.

We notice that Dr. Phipson's first note on this subject (CHEMICAL NEWS, vol. lxxi., p. 296) was entitled "The Production of Citric Acid by the Oxidation of Cane-sugar." His second note was headed "On the Production of Citric Acid from Cane-sugar." His third note, however, has the heading "Citric and Tartaric Acids from Cane-sugar," and, indeed, this note seems to be mostly concerned with the formation of tartaric acid, whilst citric acid receives very bare mention. We do not dispute the fact that tartaric acid is a product of the oxidation of cane-sugar. Many observers have confirmed this; in fact, in his second note, Dr. Phipson gives references. But Dr. Phipson appears to be diverging from the question originally at issue, namely, Can citric acid be produced by the oxidation of cane-sugar under the above conditions?

Dr. Phipson states (CHEMICAL NEWS, vol. lxxii., p. 190) that we first failed because we used too much sulphuric

acid; then, because we did not separate the organic acid by alcohol; and thirdly, because we used an insufficient quantity of permanganate (CHEMICAL NEWS, vol. lxxii., p. 190). The first and last of these objections, which have reference to the relative amounts of reagents employed, are now removed by the description of the process given by Dr. Phipson in his third note, but *still* we obtain no citric acid!

Regarding the use of alcohol for the separation of the organic acid, if it is so necessary for the success of the experiment as Dr. Phipson implies in his second note, it is strange that all mention of alcohol is omitted from his third note.

From the results of our experiments we are bound to conclude that citric acid cannot be obtained by the oxidation of cane-sugar in the manner prescribed by Dr. Phipson, and we observe that Mr. E. F. Hicks (CHEM. NEWS, vol. lxxii., p. 165) has independently arrived at the same conclusion.

67, Surrey Street, Sheffield,
November 4, 1895.

STUDY OF THE GRAPHITE EXTRACTED FROM PEGMATITE.

By HENRI MOISSAN.

WE have established in previous researches that a sufficient rise of temperature at the ordinary pressure converts every variety of carbon into graphite. We have further shown that all the graphites produced in a bath of melted metal (iron, chrome, tungsten, molybdenum, vanadium, platinum, &c.) sprout. On the contrary, the graphites obtained by the volatilisation of carbon in the electric arc or by a simple thermic transformation do not present the property of sprouting when heated after the addition of a trace of nitric acid. These researches have led us to resume the study of some natural graphites.

It is known that Berthelot has given the following definition of graphite:—"Every variety of carbon capable of yielding a graphitic oxide on oxidation."

This graphitic oxide is most commonly obtained by Brodie's method on submitting graphite to the action of a mixture of potassium chlorate and nitric acid. We observe that on projecting very dry potassium chlorate into very concentrated nitric acid it dissolves instantly with an orange-red colouration, and under these conditions, whatever variety of graphite is used, we obtain at the temperature of 60°, after an action of ten hours, an entire transformation into graphitic oxide. The slightest trace of moisture prevents this red colouration, and greatly diminishes the speed of the transformation.

The specimen of graphite which I have studied was obtained from a pegmatite from America without specification of the locality.

This pegmatite is highly interesting, since we know that this eruptive rock has reached the surface after having reached a high temperature.

In this specimen the graphite appears in fine laminar crystals, the sides of which often measure more than a centimetre, and are intimately distributed throughout the entire mass. It is easy to separate the graphite by treating the rock in its native state repeatedly in the water-bath with hydrofluoric acid at a concentration of 50 per cent. All the feldspar and silica quickly disappear. The residual matter is washed with boiling water and dried in the stove.

The pegmatite studied contained 12.77 per cent of graphite. The fine laminae thus obtained are flexible, specular, and present a surface showing striae and equilateral triangular impressions, perfectly characteristic.

This graphite takes fire in oxygen at the temperature of 690°; it yielded 5.01 per cent of ashes, composed chiefly of silica, alumina, and lime, and traces of iron.

This last metal has been detected by means of potassium sulphocyanide and ferrocyanide. The ash is white, and retains the form of the crystals of graphite. Its temperature of combustion is higher than that of the graphites of Scharzbach or of Ceylon.

This graphite sprouts. If it is moistened with monohydrated nitric acid, as Sn. Luzzi recommends, and then heated to dull redness, it sprouts abundantly.

If this graphite is treated with the oxidising mixture of potassium chlorate and of monohydrated nitric acid in large excess, there is presented a very curious phenomenon. We placed 6 grms. of graphite in a flask holding 500 c.c. along with a pinch of potassium chlorate and about 20 c.c. of nitric acid. At the outset of the reaction the graphite takes a fine greenish tint, due to a superficial reaction, and after some hours it increases in bulk in the liquid so as to fill half the flask. On a second attack it continues to sprout, and its bulk increases so that the vessel must be changed. This is the only graphite which in a liquid like nitric acid gives such an increase of volume at the temperature of 60°. After the deflagration of the graphitic oxide and its destruction, we did not find in the residue any trace of diamond, either black or transparent.

On the seventh attack with the oxidising mixture, the transformation into light green graphitic oxide is complete, but on a succeeding attack the graphitic oxide is absolutely decolourised.

On examining with a low microscopic power the fragments of quartz or of felspar to which the crystals of graphite were attached, I was much surprised to see that they presented impressions the exact image of the surface of these crystals. There are the same striæ and the same triangles, which a very energetic friction cannot remove.

This fact leads us to think that the graphite existed prior to the rocks which produced pegmatite by their crystallisation. This graphite, by its characteristic properties, completely recalls the specimens obtained in metals in a state of fusion in an electric furnace. It must have been produced under the same conditions, and at the moment of formation of pegmatite it has been moulded by the crystals of quartz and of felspar, and has left upon the latter the impression found upon its surface. — *Comptes Rendus*, cxxi., p. 538.

A NEW SPECTRAL PHOTOMETER.

By A. KENIG.

BETWEEN the collimator-tube, which has the superjacent slits always of equal width, and the eye-tube there is introduced a flint-glass prism, and further towards the eye-piece a twin-prism; that is, a combination of two flat prisms, touching each other with their thick ends (such, e.g., as are used in Fresnel's interference experiment), and towards the collimator a so-called Rochon's prism. By means of this arrangement there are produced eight spectra, in one plane of which three times two each coincide with each other, and of which each pair are polarised vertically to one another. In the plane in which the spectra appear there is a diaphragm which, at the spot where two spectra polarised vertically to each other coincide, possesses a slit, through which therefore a given colour is cut out of both prisms. If we look through the slit towards the twin prism its entire surface is illuminated with spectral light, and we see the upper half of the field of vision illuminated with light of the one spectrum, and the lower half with the light of the other. By turning the telescope we can see through the slit another colour of both spectra, so that the observation can be effected for each colour. If we have only one source of light for both slits, or if we cause two sources of light of equal brightness to act upon one of the slits, there ensues a slight

loss in consequence of the reflection within the apparatus, and the two semicircles are not equally illuminated. If we now interpose a Nicol prism between the telescope and the slit in the diaphragm upon which the spectra fall, we can produce an equal brightness of both fields of vision by turning the Nicol prism. If the sources of light which throw the light into each of the two slits are of different intensity, we can have an equal intensity by another rotation of the Nicol prism. The proportion of the illuminations can be deduced from the angle of deflection. — *Annalen der Physik und Chemie*, and *Zeit. für Analytische Chemie*.

ON THE INFLUENCE OF SALTS UPON THE BEHAVIOUR OF INVERT-SUGAR WITH THE ALKALINE SOLUTION OF COPPER.

By ARTHUR BORINTRAGER.

THE author gives an experimental study of the question whether the presence of salts has any effect upon the determination of invert-sugar by the Fehling-Soxhlet method. He concludes that of the salts which are here concerned those having a neutral reaction with litmus (sodium and potassium chlorides, sodium sulphate and acetate) have no effect upon the reductive power of solutions of invert-sugar, either immediately or on prolonged contact in the cold, or on evaporation.

On the contrary, it appears that the salts having an alkaline reaction with litmus (such as sodium carbonate and phosphate) can, by their mere presence, increase the reductive action of invert-sugar. In the case of soda, it further appeared that a prolonged action in the cold has the opposite effect, decreasing this power. Sodium phosphate has no such effect on prolonged action in the cold, but on evaporation. — *Deutsche Zucker Industrie*, 1894, pp. 1529, 1563.

DETECTION AND DETERMINATION OF CALCIUM CHLORATE IN CHLORIDE OF LIME.

By R. FRESSENIUS.

EVEN in recently-prepared chloride of lime calcium chlorate is often present when the calcium hydroxide exposed to the chlorine contained calcium carbonate. In this case hypochlorous acid is liberated, and is quickly decomposed, with formation of chloric acid. Lunge and Schoch found (*Berichte*, 1887, p. 1477) in a very carefully prepared chloride of lime 0.20 per cent of chlorine in the state of chlorate. In old chloride of lime calcium chlorate is almost always present, as appears from the experiments of Pattinson (*Forum. Soc. Chem. Industry*, 1888). He preserved specimens for a year in twelve small stoppered bottles, each holding 120 grms. at 21.1° and 26.6°, and determined every month the chlorine present in the state of chlorate in one of the bottles. The chlorine present in this state increased from 0.09 to 0.43 per cent in the samples preserved at 21.1°; and in those kept at 26.6° up to 1.37 per cent. The striking circumstance that in the former series the samples examined in April, May, June, and July contained no chloric acid; and in the second series mere traces of chloric acid were found in April and May; and that in the second series, in October 1.45 per cent, in November 1.29, and in December 1.37 of chlorine were found in the state of chloric acid might be due to the manner in which the chloric acid was determined. Pattinson added to the specimen of chloride of lime suspended in water aqueous sulphurous

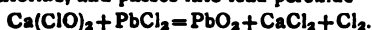
acid, heated to ebullition, added after the expulsion of the chief part of the excess of the sulphurous acid a few drops of nitric acid for its complete elimination, neutralised with calcium carbonate, determined the total chlorine by titration with silver nitrate, and subtracted from this value the sum of the chlorine present in the bleaching state and as a chloride. The small quantity of chlorine present in the state of a chlorate was calculated from the difference; that is, by a method in which the inevitable inaccuracies in the determination of the large quantity of chlorine present in the bleaching state and of the chlorine found as calcium chloride must greatly interfere with a precise estimation of the small quantity of chloric acid.

As the question often occurs to chemists whether a chloride of lime contains calcium chlorate, and if so, what quantity? I have sought to elaborate a simple procedure for its direct detection and determination.

It depends upon the fact that the hypochlorites are decomposed by lead acetate with the simultaneous formation of lead peroxide, whilst chlorates remain unchanged; it is convenient to proceed as follows:—

We grind up finely 20 grms. of chloride of lime with a little water, adding gradually more water, rinse the whole into a litre flask, fill up to the neck, shake up well, allow it to subside, filter through a dry filter-paper, and use 50 c.c. of the filtrate for the detection of chloric acid, or for its determination.

In either case we mix the measured 50 c.c. of the solution in a boiling flask with a solution of neutral lead acetate in some excess. There is formed at first a white precipitate of lead chloride and lead hydroxide, which, in consequence of the action of the hypochlorite upon the lead chloride, becomes yellow and then brown, with liberation of chlorine, and passes into lead peroxide—



When the precipitate has subsided, we add a little more solution of neutral lead acetate in order to be certain that the lead salt is present in excess, and if a further precipitation takes place we add still more of the solution of lead acetate.

We now allow the mixture to stand, preferably in an unstoppered boiling flask, with frequent agitation, when the odour of chlorine gradually disappears; in part by evaporation, but chiefly by acting upon the excess of lead acetate, forming lead chloride and peroxide and free acetic acid—



The odour of chlorine disappears completely in about eight to ten hours.

If it is merely requisite to recognise chloric acid, we filter off the precipitate, remove the lead oxide from the filtrate by adding dilute sulphuric acid in slight excess, filter, mix the filtrate with a small quantity of solution of indigo, and then add, drop by drop, a small quantity of a solution of sulphurous acid in water. If chloric acid is present, it is reduced by the sulphurous acid and the lower oxides of chlorine, or if the reduction has proceeded further the chlorine destroys the indigo blue.

That an excess of sulphurous acid must be avoided is manifest, since in that case the action of the chlorine must be annulled; the chlorine being converted into hydrochloric acid by the decomposition of water and the formation of sulphuric acid.

Of the fact that no chloric acid is formed in the above process I satisfied myself by repeatedly preparing solutions of chloride of lime by mixing chlorine water with an excess of milk of lime, filtering, and treating the filtrate with solution of lead acetate, as above directed. In the solutions of chloride of lime thus obtained no chloric acid was ever detected.

If chloric acid is to be determined quantitatively, we wash the precipitate of lead chloride and lead peroxide until the washing water has no longer an acid reaction. The washings are somewhat concentrated by evapora-

tion, added to the filtrate, the liquid is mixed with a solution of sodium carbonate in slight excess; after some time the precipitate of lead and calcium carbonates is filtered off, washed, evaporated nearly to dryness on the water-bath, introduced into a small flask, and the chloric acid is determined according to Bunsen's method, by heating with concentrated hydrochloric acid, conveying the gases given off into a solution of potassium iodide, and determining the iodine liberated with sodium hyposulphite or by Finkener's modification. Six equivalents of iodine liberated correspond to one equivalent of chloric acid.—*Zeit. f. Analytische Chemie.*

SPECIFIC VOLUME AND THE GENESIS OF THE ELEMENTS.

By C. T. BLANSHARD, M.A.

(Concluded from p. 231).

We will now enquire, though with very meagre data to work upon, what light organic chemistry has to throw on the evolution of the elements, from the point of view of differences in specific volume. All specific gravities are taken at 15° C.

Normal Primary Alcohols.

(Sp. gra. in this list and the next from Meyer and Jacobson, *Lehrbuch der organ. Chemie*, Leipzig, 1893).

Formula.	Sp. gr.	Sp. vol.	Diff.
$\text{CH}_3.\text{OH}$	0·812	39·70	17·37
$\text{C}_2\text{H}_5.\text{OH}$	0·806	57·07	16·54
$\text{C}_3\text{H}_7.\text{OH}$	0·817	73·61	16·30
$\text{C}_4\text{H}_9.\text{OH}$	0·823	89·91	16·20
$\text{C}_5\text{H}_{11}.\text{OH}$	0·829	106·1	16·3
$\text{C}_6\text{H}_{13}.\text{OH}$	0·833	122·4	16·3
$\text{C}_7\text{H}_{15}.\text{OH}$	0·836	138·7	16·2
$\text{C}_8\text{H}_{17}.\text{OH}$	0·839	154·9	17·1
$\text{C}_9\text{H}_{19}.\text{OH}$	0·842	171·0	17·3
$\text{C}_{10}\text{H}_{21}.\text{OH}$	0·839	188·3	

The differences are nearly constant.

Normal Halogen Esters.

Formula.	Sp. gr.	Sp. vol.	Diff.
$\text{CH}_3.\text{Cl}$	0·952	52·99	17·22
$\text{C}_2\text{H}_5.\text{Cl}$	0·918	70·21	15·79
$\text{C}_3\text{H}_7.\text{Cl}$	0·912	86·00	15·93
$\text{C}_4\text{H}_9.\text{Cl}$	0·907	101·93	15·94
$\text{C}_5\text{H}_{11}.\text{Cl}$	0·901	117·87	17·16
$\text{C}_6\text{H}_{13}.\text{Cl}$	0·892	135·03	17·58
$\text{C}_7\text{H}_{15}.\text{Cl}$	0·881	152·61	16·09
$\text{C}_8\text{H}_{17}.\text{Cl}$	0·880	168·70	

Differences nearly constant; with the exception of the fourth and fifth they alternate.

Normal Fatty Acids.

(Specific gravities from Landolt and Börnstein, *Phys. chemische Tabellen*, Berlin, 1894; except the last four, from Meyer and Jacobson).

Formula.	Sp. gr.	Sp. vol.	Diff.
H.CO ₂ H	1.245	36.95	18.60
CH ₃ .CO ₂ H	1.080	55.55	18.75
C ₂ H ₅ .CO ₂ H	0.996	74.30	17.46
C ₃ H ₇ .CO ₂ H	0.959	91.76	14.71
C ₄ H ₉ .CO ₂ H	0.958	106.47	16.28
C ₅ H ₁₁ .CO ₂ H	0.945	122.75	18.40
C ₆ H ₁₃ .CO ₂ H	0.921	141.15	16.23
C ₇ H ₁₅ .CO ₂ H	0.915	157.38	16.64
C ₈ H ₁₇ .CO ₂ H	0.908	174.02	9.35
C ₉ H ₁₉ .CO ₂ H	0.938	183.37	

The differences alternate, except the fourth. Ostwald, in his *Lehrbuch der Alg. Chemie*, vol. ii., *Stöchiometrie*, p. 360, &c., gives a few such tables; but they differ rather widely from these calculations, nor are they nearly so complete.

To take as an example the fatty acid series; Ostwald gives—

	Sp. vol.	Diff.
Formic acid	41.4	22.3
Acetic acid	63.7	21.7
Propionic acid.. ..	85.4	21.7
Butyric acid	107.1	23.6
Valeric acid	130.7	

According to Ostwald, and all other observers hitherto, the specific volumes of organic compounds are regarded as rising by constant increments; or, in other words, the differences between the specific volumes are regarded as approximately constant.

But we have seen that, whilst in the case of the normal primary alcohols the differences are nearly constant, there is a more marked alternation of differences in the chlorinated and oxidised series of compounds. Further, we shall find in certain fatty acid esters, and in certain aromatic series, whether chlorinated or not, the same alternation noticeable.

Normal Acetic Esters.

(Specific gravities from Landolt and Börnstein).

	Sp. gr.	Sp. vol.	Diff.
Methyl acetate ..	0.956	77.39	20.59
Ethyl	0.898	97.98	14.11
Propyl	0.910	112.09	20.18
Butyl	0.877	132.27	12.82
Amyl	0.896	145.09	

We learn from these tables of specific volumes, the most representative that I have been able to collate, that—1. Organic groups behave like the *a* and *b* groups of the elements, having their first differences high; 2. Except the fatty acid series and the chloro-benzene series.

Normal Benzene Hydrocarbons.

(Specific gravities in this and the next Table are from Beilstein, *Handbuch der organ. Chemie*, Hamburg and Leipzig, 1895).

Formula.	Sp. gr.	Sp. vol.	Diff.
C ₆ H ₆	0.884	88.21	17.42
C ₆ H ₅ .CH ₃	0.871	105.62	16.78
C ₆ H ₅ .C ₂ H ₅	0.866	122.40	15.53
C ₆ H ₅ .C ₃ H ₇	0.870	137.93	17.17
C ₆ H ₅ .C ₄ H ₉	0.864	155.10	16.21
C ₆ H ₅ .C ₅ H ₁₁	0.864	171.31	

The differences alternate, except the first.

Chlorobenzenes.

Formula.	Sp. gr.	Sp. vol.	Diff.
C ₆ H ₅ .Cl	1.126	99.87	11.42
C ₆ H ₄ .Cl ₂ , 1.2	1.320	111.29	13.96
C ₆ H ₃ .Cl ₃ , 1.2.4	1.465	125.25	5.4?
C ₆ H ₂ .Cl ₄ , 1.2.3.4	—	—	
C ₆ H.Cl ₅	1.842	135.86	

It is intelligible that in a highly oxidised series like the fatty acids, or a highly chlorinated one like the chlorobenzenes, the specific volumes should be strongly modified by the chlorine or oxygen respectively.

When I began this article—which has involved many hours' work—I had hoped to be able to demonstrate the greater or less degree of complexity of the so-called elements by comparison with specific volumes of organic substances of known amounts of complexity; but no such conclusions have been arrived at. I hope, however, that my partial success in the solution of this question may lead other workers into the field.

ON THE VAPOUR-TENSIONS OF MIXTURES OF VOLATILE LIQUIDS.*

By C. E. LINEBARGER.

(Continued from p. 232).

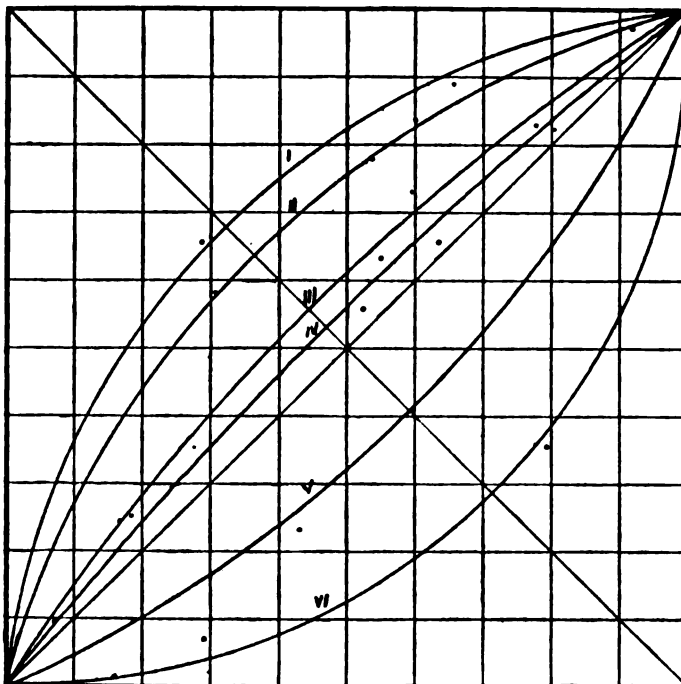
Relations between the Concentrations in the Gaseous and Liquid Phases.

THE relations between the concentration in the gaseous and liquid phases is clearly shown by curves drawn in a system of co-ordinates, of which the axis of abscissæ is taken for the representation of the molecular percentage composition of the liquid phase, and the axis of ordinates for that of the gaseous phase. These curves are drawn in the figure, the data being taken from the first two columns of tables.

As is seen, the curves prove to be very regular, and group themselves on either side of the diagonal of the square, according as the component chosen to increase from left to right in the diagram is more or less volatile than the other; as this was taken to be the component containing a halogen, the curve is below the straight line when the halogen-containing liquid is less volatile than the other, and above when it is more volatile.

Furthermore, the greater the difference in the volatility of the two liquids in the mixture the greater the curvature. It is very probable that mixtures of two normal

* Abridged from the *Journal of the American Chemical Society*, vol. xvii., No. 8, August, 1895.



RELATIONS BETWEEN THE CONCENTRATIONS IN LIQUID AND GASEOUS PHASES.

liquids with the same vapour tension would give off vapours with identical composition in both liquid and gaseous state.

Description of the Figures.

Abscissae = molecules of one liquid in 100 molecules of mixture of liquids.

Ordinates = molecules of one vapour in 100 molecules of mixture of Vapours.

- | | |
|------------------|-------------------------------|
| Curve I. | Toluene-chloroform. |
| " II. | Toluene-carbon tetrachloride. |
| " III. | Benzene-chloroform. |
| " IV. | Benzene-carbon tetrachloride. |
| " V. | Toluene-monochlorobenzene. |
| " VI. | Benzene-monochlorobenzene. |

(To be continued).

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 227).

On the Holders used for Freeing Bodies meant to be Volatilised, from Accidental Contamination by Sodium.

I PLACED on sheets of platinum, or on plates of purified carbon, plane or concave, fixed horizontally, the metallic compounds on which I wished to turn a *hydrogen and air, coal-gas and air, oxyhydrogen, or oxy-coal-gas* blowpipe jet, to free them from accidental sodium impurities. When coming to each case in particular I shall mention, with necessary details, the measures I took for attaining this end. I will say, however, that the heat and draught produced by the flame of a hydrogen and air or an oxy-coal-gas blowpipe are amply sufficient to completely eliminate the sodium; that the pressure of gas inside the blowpipe ought never to be more than *four c.m.* of water, and that as a general rule a pressure of *two c.m.* is ample.

When one exceeds a pressure of 4 c.m., as is almost always the case when using air delivered direct from a water-pump, the current carries away with it disintegrated particles of the compound, and involves thus the loss of the greater part of the body being purified.

When one uses a hydrogen and air or coal-gas and air blowpipe, the gases ought to be fed from *gasometers counterweighted* to exert the constant pressure wanted.

The same remark applies to oxyhydrogen and oxy-coal-gas blowpipes, when they are used either to eliminate the sodium contained in compounds being experimented on, or to volatilise them for the purpose of making a spectrum analysis of the flame saturated with their vapour.

On the Holders used for introducing Compounds into Flames, Electric Sparks, Electric Discharges, and Electric Arcs.

I necessarily had to adapt holders to the various conditions I had to satisfy. I will now describe shortly the arrangements I made with this object.

A. On the Clips used to introduce and Volatilise Compounds in Flames whose Temperature is less than the Melting-point of Platinum.—When it is required to introduce a compound to be vaporised into the flame of a Bunsen lamp, or into hydrogen burning in air, or into a vertical flame of a hydrogen and air or coal-gas and air blowpipe, I used an ordinary holder; that is to say, a very fine pure platinum wire, with the end simply turned up into a hook, or ending in a loop 2 or 3 m.m. diameter, or in a truncated spiral; but when I forced the jet of hydrogen burning in air, or of hydrogen and air, or of coal-gas and air, on to a compound to saturate the jet with its vapour, I placed the compound on a thin, plane or concave, plate of pure platinum. If the compound were *friable and infusible*, I collected it into a conical heap from 5 to 10 m.m. high, on a plane platinum sheet, and having made the jet *horizontal* I forced it on to the apex of the cone; when the compound was *fusible*, whether *decomposable or not* by heat, I used a very concave sheet of pure plati-

num. In the centre of the hollow I put a cone of *very porous* pure spongy platinum. The apex of the cone was from 5 to 6 m.m. above the plane surface of the platinum sheet. After having made the platinum sheet and the cone of spongy platinum red-hot, to get rid of accidental sodium impurities, I poured the melted compound on which I wished to operate over the cone, so as to completely saturate it. I then forced the jet against the apex of the cone, taking care to begin with the point of the flame and end with the hottest part.

B. *On the Holders used to introduce and Volatilise Compounds in Flames whose Temperature approaches or equals the Fusing-point of Platinum.*—The dark flame of hydrogen made incandescent by the introduction of oxygen, *without forming in it an inner cone*, and the deep blue flame of coal-gas made light blue by the introduction of oxygen, without making an inner cone, have the temperature mentioned above. For introducing a compound into these blowpipe flames, *when vertical*, I used a fine wire of pure platinum or of iridio-platinum containing 20 per cent of iridium, ending in a loop, and both overlaid with pure iridium, so as to stand a temperature considerably above the melting-point of platinum. The iridio-platinum wire was made in 1878, by Mr. George Matthey, for the use of the International Committee on Weights and Measures. The iridio-platinum alloy containing 20 per cent of iridium is as malleable and ductile as pure platinum.*

I succeeded in plating the platinum and the iridio-platinum wire with a suitable coating of white iridium, perfectly adherent and partially combined with the platinum and iridio-platinum, by powdering the wire—first moistened with glycerin—with iridium-black, and then putting it into a coal-gas and air blowpipe jet. By repeating this several times, according to the thickness wished, one can obtain wires ending in a loop or spiral, which stand perfectly well in an oxy-coal-gas blowpipe in which pure platinum wire melts. But if wires thus prepared have the advantage of resisting very high temperatures, they have the disadvantage of being brittle, or of becoming so after use, and of being very difficult to handle without breaking when one tries to make the body to be volatilised adhere to the loop, or to introduce it into the truncated spiral.

Pure platinum wire does not alter the blue flame of a Bunsen burner, but a wire of platinum overlaid with iridium gives it a persistent *violet-blue* tint; this latter wire does not alter the light blue colour of incandescent hydrogen. Spectrum analysis of this last flame shows a continuous spectrum identical with that shown by incandescent hydrogen without an iridium-covered platinum wire—a clear proof that, at this extreme temperature, iridium neither oxidises nor volatilises, as is the case at a lower temperature, just as Sainte-Claire Deville, Debray, and I have found.

One can procure iridium-black suitable for this purpose by reducing chloro-iridiate of ammonium by hydrogen or coal-gas, at the low temperature of the volatilisation of chloride of ammonium, and replacing the hydrogen by pure nitrogen as it cools.

When I had to force a *horizontal* jet of incandescent hydrogen, or the light blue jet of an oxy-coal-gas blowpipe on to a compound, in order to volatilise it, I made different arrangements, according as the body was *fusible* or *infusible*. When the body was *fusible* and *infusible* I made it into a conical heap on a plane sheet of platinum, or on a dish of purified retort carbon; when, on the other hand, the compound was *fusible*, I poured it in a melted state over a cone of very porous spongy iridium, placed in a hollow formed in the middle either of a sheet of pure platinum or iridio-platinum, or plate of purified retort carbon, the top of the spongy iridium cone being from 5 to 6 m.m. above the sheet or

plate, exactly as I have described above. It is only necessary to substitute a cone of spongy iridium for the cone of spongy platinum used in the former case.

C. *On the Clips used for introducing and Volatilising Compounds in Flames whose Temperature approaches or equals the Fusing-point of Iridium.*—The inner cone of an oxyhydrogen or oxy-coal-gas blowpipe flame, when brought to a minimum length, is at the temperature mentioned above. When I introduced a compound into the interior of the inner cone of a *vertical* blowpipe flame, I completely covered with the compound either a strong filament of purified carbon ending in a sharp point, or a small rod of iridio-platinum with 80 per cent of iridium *forged at white heat*, ending in a fine point overlaid with pure iridium.

When the carbon filament is properly covered with a compound, which remains almost entirely on the surface, it resists, before being completely burnt, a sufficient length of time to permit a spectrum analysis of the flame in which the compound is vapourised.

The small-pointed iridio-platinum rods with 20 per cent of platinum, and overlaid with pure iridium, resist much longer before melting. The pointed end bends when approaching the point of fusion, and thus tells automatically when it is necessary to remove it from the inner cone in order to save it from melting.

When I wished to force the inner cone of an oxyhydrogen or oxy-coal-gas flame, *horizontally*, or nearly so, on to a compound to volatilise it, *without contaminating the holder with sodium*, I met with great difficulties: to overcome these I had to resort to complex methods, which involved me in a long and expensive work, because it necessitated the preparation and employment of very considerable quantities of *pure white iridium*, of welded *iridium plates*, and even of a cup of *fused iridium*.

The first method consisted in the use of a flat plate of pure white iridium, 5 m.m. long, *completely* covering a disc of carbon which had been purified and freed from sodium, 3 c.m. diameter by 5 m.m. thick, let in, to the depth of 6 m.m., to a hole made in a small block of pure magnesia compressed and hardened by being exposed to a white heat, made by the late Colonel Caron. The magnesia block, before receiving the carbon disc, was heated for some time in a coal-gas and air blowpipe, to drive off the sodium obstinately held by magnesia even when it is free from silicic acid.

Having warmed the white iridium plate, which was raised from 2 to 3 m.m. above the top of the block of magnesia, in a coal-gas and air blowpipe, until all the sodium deposited by the air was driven off, I put in the middle of the plate, with platinum forceps, a small iridium dish, which had been welded in an oxy-coal-gas blowpipe flame, carrying either a core of an infusible compound or a hollow core of welded iridium, covered externally with the compound (oxychloride, sulphate, or carbonate) that I wanted to put into the inner cone of an oxyhydrogen or oxy-coal-gas blowpipe, in order to volatilise it and make a spectrum analysis of its vapour.

The second method consisted in replacing the plate of white iridium, permeable by liquids, by a cup of fused iridium, not permeable by liquids, let in for half its height to a small block of pure magnesia, compressed and hardened at a sustained white heat, and heated in an oxy-coal-gas blowpipe until accidental sodium impurities were entirely driven off. The fused iridium cup was 3 c.m. diameter by 8 m.m. high. It was dished in the centre to a depth of 4 m.m., and weighed 102.800 grms. I owe the possession of this unique cup—without which it would have been impossible to raise the vapour of potassium, sodium, and lithium compounds to the temperature of the inner cone of an oxyhydrogen blowpipe flame—to the kindness of Mr. G. Matthey. When I used the cup, a hollow cone of welded iridium was put in the bottom of it. The top of this cone was about 2 m.m. above the edge of the cup. Having raised the cup and the contained cone in an oxy-coal-gas blowpipe flame to

* "Report of the International Committee on Weights and Measures." Meetings during 1878; Paris 1879.

a temperature near the fusing-point of platinum, I filled it with the liquid compound meant to be volatilised; at the same time I turned the inner cone of an oxyhydrogen blowpipe flame on to the top of the cone saturated with the liquid, whilst, with a conveniently placed spectroscop, M. Rommelaere and I proceeded with the spectrum analysis of different parts of the flame charged with vapour. It several times happened that, on turning an oxyhydrogen blowpipe flame on to the top of the iridium cone in the iridium cup containing an alkaline chloride or sulphate heated to the fusing-point of platinum, these compounds exploded, and were thrown to some distance, scattering fiery drops about. To guard ourselves from danger, and to protect our instruments, we covered ourselves and the spectroscopes with wet cloths.

Iridium undergoes no alteration by contact with chlorides and sulphates of potassium, sodium, and lithium, or even lithium oxide, when raised to the highest temperature attainable in an oxyhydrogen blowpipe flame. On the other hand, compounds of calcium, strontium, and barium always attack the surface of iridium, whether welded or fused. It produces thus at first coloured compounds, containing calcium, strontium, and barium. These compounds decompose finally, leaving the iridium with a roughened surface.

I cleaned the articles which had been used in experiments by treating them first with very dilute hydrochloric acid, and then by keeping them for at least one hour in a mixture of equal parts of anhydrous bisulphates of potassium and sodium at a dull red heat. After having washed them thoroughly with water, I heated them in a coal gas and air blowpipe flame, until they showed no trace of the spectrum of the compound which had been in contact with the iridium.

(To be continued).

THE QUANTITATIVE DETERMINATION OF PERCHLORATES.*

By D. ALBERT KREIDER.

THE method usually employed for the quantitative determination of perchlorates, by igniting to the chloride and weighing the halogen as the silver salt, is indirect and subject to error, especially as my experience proved, where the free acid is to be determined, and where, consequently, an alkali which is apt to contain chloride is used to form the salt for the ignition. To purify the salt for this method only adds to the complication, and therefore a more satisfactory process was sought. In a recent article (*Amer. Journ. of Science*, vol. xlviii., p. 38) from this laboratory, by Prof. Gooch and myself, a method for the detection of alkaline perchlorates associated with chlorides, chlorates, and nitrates was detailed, with mention of certain efforts towards a quantitative determination. As throwing light upon the peculiar properties of perchlorates, and as an introduction to the satisfactory method which I have finally developed, some of the results of these earlier efforts will here be given.

In studying the properties of perchloric acid in the form of its potassium salt, we found that when treated with potassium iodide in the presence of boiling phosphoric acid, no reduction of the perchlorate is effected,—unless indeed, the boiling be continued till the temperature rises to 215° to 220° C., where the meta-phosphoric acid begins to form. But when the meta-phosphoric acid (made by heating the syrupy ortho-acid to 360° C.) is directly applied in the presence of potassium iodide, and kept at a temperature of about 200° C., iodine is copiously evolved. To test this reaction quantitatively, a number of experiments were made in an apparatus consisting of a retort,

into the tubulature of which a glass tube was carefully ground and prolonged so as to reach to the bottom of the bulb and serve for the passage of a current of carbon dioxide, used to expel the air and carry the iodine into the receiver. The neck of the retort was bent so as to reach to the bottom of an Erlenmeyer receiving vessel, containing a solution of potassium iodide, which was trapped by a side-necked test-tube. After introducing the perchlorate with the iodide and meta-phosphoric acid, all air was expelled by carbon dioxide and heat applied. The iodine collected in the receiver was titrated with decinormal thiosulphate, from which the perchlorate was calculated.

Table I. gives the results of several experiments performed in this way, which prove that even with a large excess of potassium iodide the perchlorate is so slowly reduced that the hydriodic acid escapes before the reduction is completed. In order to delay the distillation of hydriodic acid until the perchlorate had been completely reduced, the potassium iodide of experiment (3) was introduced in a short tube sealed at one end, so that the meta-phosphoric acid could attack it only slowly, and the heat quickly raised to about 300° C, but evidently without advantage. In experiment (4) the iodide was introduced in the same way, but the heat was applied gradually and more moderately, with considerably improved results.

TABLE I.

	KClO ₄ taken. Grms.	HOPO ₃ used. C.m.s.	KI used. Grms.	KClO ₄ found. Grm.	Error. Grm.
(1)	0.1000	15	5.0	0.0741	0.0259—
(2)	0.1000	17	10.0	0.0844	0.0156—
(3)	0.1000	15	5.0	0.0364	0.0636—
(4)	0.1000	15	5.0	0.0977	0.0023—

A complete reduction of the perchlorate evidently necessitated the means of introducing the iodide in sufficient quantity and at will.

For this purpose the tube serving for the introduction of carbon dioxide was enlarged so as to hold the iodide, which could then be added to the solution at any time by a manipulation of the rubber conducting-tube for carbon dioxide, which would draw the acid up to the iodide, and, retreating, would carry back an easily regulated quantity of the latter.

TABLE II.

	KClO ₄ taken. Grm.	KI used. Grms.	KClO ₄ found. Grm.	Error. Grm.
(5)	0.1000	5.0	0.0984	0.0016—
(6)	0.1000	3.0	0.0924	0.0076—
(7)	0.0500	2.0	0.0508	0.0008+
(8)	0.0500	2.0	0.0479	0.0021—
(9)	0.1000	7.0	0.0977	0.0023—
(10)	0.1000	3.0	0.0925	0.0075—
(11)	0.1000	3.0	0.0999	0.0001—
(12)	0.1000	2.0	0.0994	0.0006—
(13)	0.1000	4.0	0.0966	0.0034—

Table II. gives a number of results obtained in this way. Experiments (10), (11), and (12) differed from the others only in the employment of a bulb pipette instead of the retort; one end being bent so as to reach to the receiver, and the other cut off rather short with a tube ground into it, serving the same purpose of conducting carbon dioxide and holding potassium iodide—the greater inclination of the potassium iodide tube made possible by this change appearing to offer advantages for the more gradual and regular introduction of the iodide. The amount of meta-phosphoric acid used was in all cases 15 c.m.s. In experiment (13) heat was applied by means of a bath kept at 230°.

While several of these determinations gave only admissible errors, the irregularity of the remainder, and the uncertainty in striking just the proper conditions for good results, proved the method worthless, at least in that shape.

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. 1., October, 1895.

The experiments of Table III. record the results of adding the acid drop by drop to an intimate mixture of the powdered perchlorate and iodide kept hot.

TABLE III.

	KClO ₄ taken. Grm.	KI taken. Grms.	KClO ₄ found. Grm.	Error. Grm.
(14)	0.1000	4.0	0.1036	0.0036+
(15)	0.0500	2.0	0.0502	0.0002+
(16)	0.0500	3.0	0.0515	0.0015+

The high results of this Table doubtless point to the dissociation of hydriodic acid or to the partial reduction of the meta-phosphoric acid in the temperature, which would naturally rise higher where so small an amount of liquid was present. But when the meta-phosphoric acid was there in greater amount, the distillation of the hydriodic acid before the complete reduction of the perchlorate could not be prevented.

An ordinary mixture having thus been found insufficient to hold the hydriodic acid to the reduction of perchlorates, a search for some compound in which the perchlorate could be fused with an excess of potassium iodide and the mixture thus obtained subjected to the action of meta-phosphoric acid resulted in the employment of zinc chloride. Anhydrous zinc chloride was found to fuse at about 200° C. The perchlorate and iodide could be added to this fusion, and the whole melted, thoroughly diffused and cooled, without any evolution of iodine. This mass, when treated with meta-phosphoric acid in the apparatus previously employed, melted gradually with a copious evolution of iodine.

Table IV. shows the quantitative action. The amount of zinc chloride used was roughly taken about equal to that of the iodide.

TABLE IV.

	KClO ₄ taken. Grm.	KI taken. Grms.	KClO ₄ found. Grm.	Error. Grm.
(17)	0.0500	5.0	0.0552	0.0052+
(18)	0.0000	5.0	0.0044	0.0044+
(19)	0.0000	4.0	0.0057	0.0057+

In (19) a mixture of cadmium iodide and potassium iodide, taken in the proportion of their molecular weights, was substituted for the zinc chloride. The known salt corresponding to the formula $\text{CdI}_2 \cdot 2\text{KI} + 2\text{H}_2\text{O}$ was not so convenient, because of its high melting-point—230° C.; but when the two iodides are taken in the proportion of their molecular weights, the mixture fuses at about 200° C. Although this mass, after fusion, was more easily soluble than the zinc residue, the blank determination revealed a source of error equally disparaging.

Gaseous hydriodic acid passed into a mixture of the perchlorate and meta-phosphoric acid at a temperature between 200° and 300° C., was markedly less effective than the generation of the acid on the spot; and the distilling of the perchloric acid by meta-phosphoric acid into a receiver of potassium iodide yielded only a trifling amount of iodine, while the passage of hydriodic acid over the fusing perchlorate in a short combustion tube was precluded by the high melting-point of the perchlorate endangering the dissociation of the halogen.

The invariably high results obtained by the use of meta-phosphoric acid in all those experiments in which there was a reasonable assurance that the hydriodic acid was held till the perchlorate was completely broken up—experiments (13), (14), (15), (17), (18), and (19)—indicated either a dissociation of hydriodic acid or a partial reduction of the meta-phosphoric acid. Of the latter cause there were some grounds for suspicion, but, as its determination led too far from the object of the investigation, the use of phosphoric acid was abandoned. So far as our experience extended there remained, then, nothing among the reagents of the wet methods which was sufficiently active and stable enough to warrant its application. Fusion alone seemed capable of extracting the oxygen

from the perchlorate. A number of preliminary tests were therefore made on certain salts of the halogens, in the hope of finding one which would be acted upon by the oxygen of the perchlorate with the liberation of the halogen, which latter could be collected in a receiver of potassium iodide and titrated with thiosulphate.

The double chloride of aluminum and sodium, $\text{Al}_2\text{Cl}_6 \cdot 2\text{NaCl}$, melts at about 200° C., and was in other respects desirable. When fused with potassium perchlorate, chlorine was copiously evolved. The action of air on the fusion also liberated chlorine; but blank determinations in an atmosphere of carbon dioxide proved that under these conditions not a trace of chlorine was evolved. The apparatus employed for a quantitative test of this reaction on perchlorates consisted of a small distilling flask of about 20 c.m.³ capacity, into the tubulature of which was ground a piece of glass tubing reaching well into the bulb, and serving for the passage of carbon dioxide. The side neck was sealed to one of two connected Will and Varrentrapp absorption bulbs containing a solution of potassium iodide to receive the chlorine. After weighing the perchlorate into the flask, and adding a sufficient amount of the powdered double chloride, all air was expelled by carbon dioxide, and heat applied till the fused mass was raised considerably above the melting-point and kept there for some time. Table V. contains the results of a number of experiments performed in this way.

TABLE V.

	KClO ₄ taken. Grm.	KClO ₄ found. Grm.	Error. Grm.
(20)	0.0500	0.0438	0.0062—
(21)	0.0500	0.0482	0.0018—
(22)	0.0500	0.0460	0.0040—
(23)	0.1193	0.1175	0.0018—
(24)	0.1039	0.1018	0.0021—
(25)	0.0500	0.0477	0.0023—
(26)	0.1003	0.0946	0.0057—

These results came so close to being quantitative that a little help in the form of free acid seemed all that would be necessary to complete the reaction. But the addition of meta-phosphoric acid to the cooled mass after the fusion in (22) gave no additional evolution of iodine. In (25) gaseous hydrochloric acid was passed in with the carbon dioxide in the hope of meeting the deficiency, but was evidently no improvement. One test, in which meta-phosphoric acid was added to the fusion, resulted in such a violent evolution of hydrochloric acid that the whole contents of the flask was forced into the receivers.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, November 8th, 1895.

Prof. A. W. RÜCKER, Vice-President, in the Chair.

MR. W. H. EVERETT read a paper on "*The Magnetic Field of any Cylindrical Coil or Plane Circuit.*"

The method of treatment is based on the formula for the force due to an element of current. A single integration applied to one component of this force gives for any point in the field due to a plane circuit the force perpendicular to its plane; and a double integration gives the longitudinal force at any point due to a cylindrical coil of any cross-section, the depth of winding being supposed inconsiderable. For coils in which the latter condition does not hold, an approximate solution can readily be found. The force parallel to the plane of a circuit, and the transverse force due to a coil, are investigated in a

similar manner. The general results are of a very simple form and admit of easy approximate calculation. Special formulæ are deduced for coils of rectangular cross-section, the general expressions being in this case integrable.

Appended to the paper are some numerical results giving the values of the forces at different points due to coils of various dimensions.

Prof. PERRY said he considered the paper to be a valuable one, particularly as illustrating a practical mathematical method of integrating.

Mr. TROTTER said the paper was of interest to him, as he considered that several of the author's results might be applied to the solution of problems on illumination, *cf.*, the illumination of a room by a circle of lamps.

Mr. RHODES regretted that it had not been possible to supply a proof of the paper before the meeting. The method in which the author obtained the force outside a solenoid as the difference of the forces due to two solenoids reminded him of the method employed in calculating the attraction of, say, a truncated pyramid.

Prof. SILVANUS THOMPSON said the author had mentioned several previous papers on the subject, but had not referred to one by Prof. Viriamu Jones, in which the force due to a solenoid is obtained in terms of elliptic integrals. Another method of attack was to calculate the work done when a unit pole is carried through the solenoid and back outside to the starting-point.

Prof. AYRTON said he also regretted the absence of a proof of the paper. He considered it of great importance to have exact and simple methods of calculating the forces due to a solenoid.

The Chairman (Prof. RÜCKER) said he had made a somewhat similar calculation in connection with the magnetic effect of sheets of basalt below the surface of the earth.

Mr. E. H. GRIFFITHS read a paper, by himself and Miss DOROTHY MARSHALL, on "*The Latent Heat of Evaporation of Benzene.*"

The method employed is similar to that used by one of the authors in the determination of the latent heat of evaporation of water (*Phil. Trans.*, 1895). The loss of heat due to the evaporation is balanced by (a) the heat supplied by an electric current; (b) a secondary supply due to the work done by the stirrer; (c) a slight gain or loss due to small unavoidable changes in temperature of the calorimeter. The comparative values of the various sources of heat (if we denote the supply due to the electrical current by 1000) is approximately:—Electrical = 1000; stirring = 11; changes in calorimeter temperature, ± 5 . The electrical supply could be measured with extreme accuracy, and the above table shows that small errors in the determination of the remaining thermal quantities are of little importance. The results may be summed up in the formula—

$$L = 107.05 - 0.1581 \theta;$$

where θ is the temperature, and the thermal unit at 15°C . is used.

The discussion on this paper was postponed till after the reading of the following paper.

"On a Method of Comparing the Heats of Evaporation of different Liquids at their Boiling-points." By Prof. RAMSAY and Miss MARSHALL.

The method employed has already been described before the Society (Jan. 11th, 1895). The liquid to be experimented on is put into a glass bulb enclosed in an outer jacket filled with the vapour of the same liquid. An open tube is attached to the top of the bulb, so that there is free communication between the interior and the vapour-jacket, and no loss of material. Inside the bulb is a spiral of fine platinum wire, attached to stout platinum terminals which are sealed into the glass. The temperature of the liquid in the bulb is raised to the boiling-point by the vapour-jacket; thus when a current is sent through the wire the whole of the heat developed is spent in converting a portion of the liquid into vapour.

Two such bulbs are connected in series, and the ratio of their losses of weight is the inverse ratio of the heats of evaporation of the liquids. A correction is made for the inequality in resistance of the spirals, and the ratio of the differences of potential between the ends of the spirals, when the current is passing, is determined in each experiment by Poggendorff's method. Results are given for fourteen liquids.

Prof. RAMSAY drew special attention to the table giving the values of the quotient $\frac{ML}{T}$, where M is the molecular weight, T the absolute temperature, and L the latent heat. Very curious differences are noticeable in the case of water, alcohol, and acetic acid.

Prof. CAREY FOSTER expressed his admiration for the method, since it obviated the necessity of knowing the specific heat of the liquid or vapour.

Prof. SILVANUS THOMPSON said the difficulty experienced in the case of water, due to electrolysis, might be obviated by the employment of a spiral of lower resistance and a larger current, so that the difference of potential between the ends of the spiral should be less than 1.7 volts.

The CHAIRMAN said Captain Abney had asked him to enquire to what extent the temperature of the liquid was affected by radiation.

Mr. J. W. RODGER asked if any direct experiment had been made to determine if the temperature of the liquid was not above its true melting-point. In some cases differences of as much as 2° might exist between the temperature of the liquid and that of the vapour given off.

The differences in the value of $\frac{ML}{T}$ in the case of water, alcohol, and acetic acid might be due to the fact that the vapours of alcohol and water were simple, while the vapour of acetic acid was complex.

Mr. R. APPELYARD suggested that the differences obtained in the case of water might be due to the presence of dissolved air.

Mr. GRIFFITHS said that the objection to the adoption of Prof. Thompson's suggestion was the fear that, with short wires, an excessive difference in temperature between the wire and the liquid might exist.

Mr. RHODES asked if Mr. Griffiths could trust his determinations of temperature to $\frac{1}{10000}$ th of a degree?

Mr. GRIFFITHS, in reply, said that he thought there was no limit to the accuracy with which a difference of temperature could be measured; the absolute temperature, however, he only relied upon to $\frac{1}{10000}$ th of a degree.

Prof. RAMSAY said the fact of superheating existing would not affect the results, since near the temperatures at which they were working the latent heat did not vary appreciably with the temperature. In reply to Captain Abney, he said some previous experiments by Dr. Young and himself had shown that the vapour-jacket was quite impervious to radiant heat from without.

Royal Institution.—The Christmas Course of Lectures, adapted to a juvenile auditory, at the Royal Institution, will be delivered this year by Professor John Gray McKendrick, M.D., LL.D., F.R.S., Professor of Physiology in the University of Glasgow, and formerly Fullerian Professor of Physiology in the Royal Institution. The subject will be "Sound, Hearing, and Speech," and the Lectures will be experimentally illustrated. The first Lecture will be delivered on Saturday, December 28th, at Three o'clock, and the remaining Lectures on December 31st, 1895, and on January 2nd, 4th, 7th, and 9th, 1896.

Illuminating Apparatus for observing the Changes of Colour in Volumetric Analyses.—This apparatus has been constructed by A. Lupp, and can be obtained from Kähler and Martini, of Berlin. In principle it is like an arrangement often employed in dissecting microscopes.

NOTICES OF BOOKS.

Aids to the Analysis of Food and Drugs. By T. H. PEARMAIN and C. G. MOORE, M.A., F.C.S., Members of the Society of Public Analysts. London: Baillière, Tindall, and Cox. Pp. 160.

THIS little book at once commends itself to our good wishes by its Preface. The authors say:—"This work is not intended to be used as a cram-book for examination purposes. We cannot emphasise too strongly the fact that food analysis is not to be taught in a few weeks, as is frequently attempted in the interest of public health students. A competent knowledge of the analysis of food and drugs is only to be obtained by some years of active practical laboratory work."

In treating of the analysis of milk, the authors remind us that the disgraceful state of the milk trade in this country is fostered, if not actually created, by the "absurdly low standard" adopted by the Somerset House chemists who have been constituted the referees in adulteration cases. They have fixed upon 2.75 per cent as the minimum for fat, and 8.5 for "solid not fat." If we compare this standard with that adopted elsewhere, we find that it is exceptionally low. The State of New York requires fat 3 per cent; New Jersey demands total solids 12; in Massachusetts the standard is 13 solids; and in Berne total solids 12.5, and fat 3.5.

But there are other, and not less grave, errors in the "Sale of Food and Drugs Act." Its scope needs to be enlarged, so as, e.g., to bar the way to such quibbles as the well-known plea that baking powder was neither food nor a drug. The penalties are most absurdly low, and have merely a maximum limit which magistrates can and do at times reduce so as to render the punishment of the sophisticator practically nil.

In the matter of vinegar the authors seem to participate in the common English notion that this condiment should be made from malt. Now the nitrogenous matter in malt or other grain cannot at all contribute to the production of vinegar. It seems not improbable that the presence of dextrine tends to prevent the formation of those ethers which constitute the aroma of wine-, cider-, and sugar-vinegars. This theory, which merits experimental investigation, would account for the flatness of malt-vinegar.

As regards pepper, it would be well if the importation of "poivrete" and of its raw material—to wit, olive-stones—were totally prohibited. The estimation of the woody fibre seems to be a capital point in the analysis of peppers. The presence of lead chromate in any substance intended for introduction into the human system is a crime for which no money penalty is at all adequate.

The analytical procedures here recommended are trustworthy, and indicate that the authors are not compilers, but men of experience.

The Splash of a Drop. By Prof. A. M. WORTHINGTON, M.A., F.R.S. Being the Reprint of a Discourse delivered at the Royal Institution of Great Britain, May 18th, 1894. Published under the Direction of the General Literature Committee. London: Society for Promoting Christian Knowledge. 1895. Crown 8vo., pp. 76.

THE curious work before us discourses on the phenomena observed when a drop of water falls into milk; of a drop of mercury falling upon a hard, polished surface; and of a drop of milk falling upon smoked glass. The author treats only of the mechanical phase of the question, leaving, for the present at least, the electrical aspect to other investigators, such as Lenard and J. J. Thomson. As to any possible chemical phenomena produced, the author is silent.

Prof. Worthington has succeeded in reproducing the effects produced by means of the instantaneous photo-

graphic process. Thus the illustrations show, e.g., the appearances respectively 0.0262, 0.0391, and 0.101 second after the contact of a drop of water with a surface of milk. Some of these figures decidedly remind us of the lunar craters as seen with the telescope.

Principles and Practice of Agricultural Analysis. A Manual for the Estimation of Soils, Fertilisers, and Agricultural Products. For the Use of Analysts, Teachers, and Students of Agricultural Chemistry. Volume II.—*Fertilisers.* By HARVEY W. WILEY, Chemist of the U.S. Department of Agriculture. 8vo., pp. 332. Easton, Pennsylvania: Chemical Publishing Co. 1895.

THE appearance of this work is a striking proof of the great and enlightened attention paid to agriculture by the Government of the United States. The author's object has been "to present to the busy worker a broad view of a great subject." Those who merely want a book for routine work or in preparing for an examination are warned that they will here find little to attract them.

The present volume comprises four parts. The first treats of phosphates and phosphatic manures; the second is concerned with nitrogen in manures and their components; the third discusses potash as a manurial constituent; and the fourth speaks of such minor fertilising materials as lime, gypsum, common salt, copperas, and wood-ashes.

It will be at once seen that Mr. Wiley, like most British agricultural chemists, but unlike an eminent French authority, is far from placing lime in any form in the same rank as the three great plant foods—nitrogen, phosphates, and potash. Whilst giving the general preference to the molybdc method, Mr. Wiley points out certain sources of error which must be avoided; such as the occlusion of silica. One method of evading this difficulty is dissolving the original substance in sulphuric acid with a little nitric acid. Silica is not soluble in hot concentrated sulphuric acid. Error may, though rarely, arise from the presence of arsenic, and more frequently from the occlusion of magnesia and the volatilisation of phosphoric acid.

Basic phosphoric slags have come into such extensive use that they have attracted the notice of sophisticators. Hence their analysis, and the detection of adulterations (some of which have been actually patented!), becomes an important question. It must be noticed that the substance known in Europe as Thomas slag is called in America "odourless phosphate."

For the determination of nitrogen in manures and their crude materials, the author gives the process of Dumas, available in all cases, but now rarely used except as a check; the soda-lime process of Varrentrapp and Will, very generally used until of late for the determination of nitrogen not in the nitric form; and the Kjeldahl method, also not available for nitric nitrogenous bodies. The process of Wanklyn is pronounced to be of no practical use whatever.

For the detection of potash in manurial matters, we find mention of a spectroscopic method. Potassium gives three faint and rather broad bands, two red bands, and one of a plum colour. If these bands are not detected, we may at least conclude that the substance does not contain a ponderable quantity of potash. In addition to the ordinary platinum chloride method for the determination of potash in its various modifications, we find the process for its estimation as perchlorate, which is pronounced quite as accurate as the platinum process, simpler, more expeditious, and cheaper.

Mr. Wiley expresses the hope that deposits of potassium salts may be discovered in the United States.

The fourth part of this excellent work treats of miscellaneous fertilisers. The author considers—in our opinion, rightly—that a soil good enough to grow crops will contain sufficient lime to furnish that ingredient of plant

food for many years. The action of lime is certainly most favourable to those plants which are of value to men, whilst the plants which avoid lime, though often very beautiful, such as the heaths, azaleas, &c., are of little economical value.

We are struck with a passage to the effect that lime is not capable of acting as a fungicide. "As a rule fungi prefer acid reaction in the substances in which they grow." With the morbid microbia this rule hardly applies. Most disease germs seem to prefer an alkaline medium. Thus the use of liquids containing a trace of sulphuric acid seems a safeguard against the infection of Asiatic cholera. Yellow fever, on the contrary, prefers an acid habitat.

Gypsum, it appears, has the strange synonym of "land-plaster."

Under the name "Stall manures," the author includes farmyard manures, night-soil, the excreta of poultry, &c. Mr. Wiley very truly declares that such manures have a higher manurial value than is deducible from the proportions of phosphorus, nitrogen, and potash which they contain (p. 311). This opinion we can confirm from our own observations, and we must regret that it has been ignored by many authorities in pronouncing on the value, e.g., of sewage manures.

Mr. Wiley's work must be regarded as a splendid contribution to the chemistry of agriculture.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxi., No. 18, October 28, 1895.

Lord Kelvin, as a Foreign Associate of the Academy of Sciences, read the Address of the Royal Society of London congratulating the Institute of France on its centenary, and further delivered a speech recognising France as his *alma mater* of science.

On the Chemical Equivalents.—M. Margfroy.—The actual equivalents of chemistry are the prime numbers comprised in the natural series of whole numbers between 1 and 300. The author gives a table of his new equivalents in columns parallel with the present equivalents and the atomic weights. The equivalents of boron and sulphur he makes identical, as also those respectively of magnesium and glucinum, of chrome and palladium, of tin and cobalt. That of nickel he makes 149, as against the equivalent 29·5 at present accepted. Gold and platinum he makes alike, as also tungsten and lanthanum, and iridium and osmium. The number of prime numbers which exist among the 300 whole numbers is 63. M. Margfroy adds that he has established the constitutive theory of substances founded on the unity of matter, he introduces into the consideration of the volumes the element of porosity, and thus succeeds in combatting the law of Dulong and Petit and the hypothesis of Avogadro. He puts forward the following law:—The specific heat multiplied by the density is equal to the porosity, the porosity of hydrogen under the existing conditions of temperature and pressure being taken as unity.

Thermo-chemical Researches on Lithium, Magnesium, and Copper Cyanides.—Raoul Varet.—The author's results are that the heat evolved from Li in solution with gaseous cyanogen and water is +65·12 cal.; that from magnesium under the same conditions is +112·0 cal.; and that for copper +29·8 cal.

Glucinum Carbide.—Louis Henry.—If we ascribe to glucinum the atomic weight 9·03, and to carbon that of

11·97, glucinum carbide must be represented by the formula CGl . Lebeau's investigation gives us no reason for modifying the atomic weight and the valence generally attributed to glucinum.

Analysis of Emerald.—P. Lebeau.—The author has operated on the emerald of Limoges (Chanteloube, Haute Vienna). He gives the following results:—

	I.	II.
Loss at a red heat	1·46	1·41
Silica	66·06	65·80
Alumina	16·1	16·40
Glucose (? should be glucina) ..	14·33	14·21
Ferric oxide	1·2	0·9
Mn_2O_4	—	—
Magnesia	0·55	0·61
Lime	0·17	0·14
Phosphoric acid	0·11	0·09
Alkalis	—	—
Titanic acid	traces	traces
	100·11	99·67

Determination of Argon.—Th. Schlösing, jun.—This paper will be inserted in full.

Synthetic Formation of a New Ketonic Acid.—E. Burkner.—The compound in question has been obtained by the action of camphoric anhydride upon benzene in presence of aluminium chloride. Its composition is $C_{15}H_{20}O_2$. It forms white crystals of a nacreous lustre which melt at 135–137° and boil at 320° at a pressure of 760 m.m. They are almost insoluble in water, sparingly soluble in ligroine, but readily soluble in acetic acid, alcohol, ether, benzene, chloroform, and carbon disulphide. The author has formed and examined its ammonium, barium, silver, copper, cobalt, nickel, zinc, and lead salts. He has also obtained its ethylic and methylic ethers, its anhydride, amide, and hydrazide.

Liquefaction of Gelatin; its Saline Digestion.—A. Dastre and N. Floresco.—Gelatin is transformable into a kindred substance, gelatose or protogelatose, characterised by want of the property of forming a jelly and of being precipitated by a standard solution of sodium chloride. In cultures of liquefactive microbia it is observed in the first moments that the gelatin is changed into gelatose. Gelatin loses the property of jellifying if left in contact with an alkaline chloride or iodide. With the fluorides, the transformation is only partial. The change may be named saline digestion.

Zeitschrift für Analytische Chemie.
Vol. xxiv., Part 2, 1895.

Researches on the Amorphous Nitrogenous Organic Compounds present in Beer Wort.—H. Schjerning.

Determination of Sulphurous and Sulphuric Acids in the Products of the Combustion of Coal-gas.—Uno Collan.—The author hopes to have demonstrated that the sulphur of coal-gas, both in the luminous and in the non-luminous flames, is chiefly converted into dioxide.

Demonstration of the Blood-spots in Judicial Investigations.—M. Gantter.—(See vol. lxxi., p. 238).

Improvements in Glass Cocks.—H. Wolpert.—This paper requires the nine accompanying figures.

Retardation of Ebullition, and on the Ejection of Liquids.—H. Wolpert.

New Burner for Sodium Light.—Richard Pribram.

Simple Apparatus for Extraction.—Richard Pribram.

Apparatus for Measuring off Small Quantities of Mercury in the Kjeldahl Nitrogen Process.—Paul Liechthli.—These three above papers cannot be intelligibly reproduced without the accompanying figures.

Determination of Antimony as Antimonie Antimoniate.—Otto Brunek.—Already inserted.

Examination of Butter.—Carl Th. Möerner.—The author finds the baryta number for twenty samples of fresh butter from Central and Southern Sweden on the average 200.7, *i.e.*, a little lower than the values obtained by König and Hart.

Introduction to Microchemical Analysis.—H. Behrens.—This work is noticed in a brief but highly laudatory manner.

Use of the Electric Current as a Source of Heat.—A conspectus of the methods devised by Saladin (*Soc. Chim. de Paris*), Ducretet and Lejeune (*Ibidem*), H. Moissan, Jules Violle, and Lagrange, and Hohe (*Comptes Rendus*).

Sources of Current, Resistance, and General Arrangements for Electrolysis.—A compilation including notices of a new dynamo for metallurgical laboratories and lecture rooms, by W. Borchers (*Comptes Rendus*).—As the most convenient source of electricity for chemical laboratories Karl Elbs (*Chemiker Zeitung*) recommends accumulators which may be readily charged by a Gülcher thermo battery of 66 elements. Felix Oettel (*Chemiker Zeitung*) shows that in directions for the electro-deposition of metals it is necessary to specify the strength of the current per unit of surface; as such unit he selects the square decimetre. Communications follow by J. S. Stillwell and Prof. P. T. Austen on the use of electric lamps in electrolysis. The authors use glow-lamps as resistances, which, as the Editors point out, is no novelty. The contents of Rüchhoff's paper are purely polemical.

Use of Sound Vibrations in the Analysis of Gaseous Mixtures.—E. Hardy.—From the *Comptes Rendus*.

Apparatus for Purifying Oxygen and Air in Elementary Analysis.—Hugo Schiff.—A description of the apparatus would require the two accompanying figures.

New Urometer.—Th. Lohnstein (*All. Med. Central-Zeitung*).—A special form of hydrometer.

Some small Laboratory Apparatus.—André Bidet.—These appliances cannot be satisfactorily described without the accompanying figures.

Motor for Laboratory Purposes.—Ewald Saur.—This apparatus is an application of Henrici's hot-air motor, and cannot be described without the illustration here given.

New Cock for Vacuum Exsiccators.—O. Ernst.

Determination of Carbon in Iron.—A critical compilation of known methods.

Distinction between α - and β -Naphthols.—Aymonier (*Repert. Pharm. and Zeit. des Allgem. Oesterr. Apotheker Vereins*) uses a solution of 1 grm. of potassium dichromate and 1 grm. nitric acid in 100 c.c. of distilled water. If a few drops of this solution are added to an aqueous or dilute alcoholic solution of the naphthols there appears a black precipitate in the absence of α -naphthol.

MEETINGS FOR THE WEEK.

WEDNESDAY, 20th.—Society of Arts, 8. Opening Address of the 142nd Session, by Major-General Sir John Donnelly, K.C.B., Chairman of the Council.

THURSDAY, 21st.—Chemical, 8. "The Evolution of Carbon Monoxide by Alkaline Pyrogallol Solutions during Absorption of Oxygen," by Prof. Clowes. "The Composition of the Limiting Explosive Mixtures of various Combustible Gases with Air," "Barium Butyrate, and the Estimation of Butyric Acid," by W. H. Willcox. And other papers.

FRIDAY, 22nd.—Physical, 5. An Exhibition of Photographs of Spectra, by G. Johnstone Stoney. "A Direct-reading Platinum Thermometer," by R. Appleyard. "Historical Note on Resistance and its Change with Temperature," by R. Appleyard.

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THE CHEMICAL NEWS.

VOL. LXXII., No. 1878.

ON ARGON.

By R. NASINI.

THE author is of opinion that the monatomic character of argon, as deduced from the kinetic theory of gases, cannot yet be regarded as irrefragably established. If the kinetic theory of gases allows us to predict for monatomic gaseous molecules with great probability a value for k approximating to 1.67 (k being the relation of the specific molecular heat at a constant pressure to the specific heat at a constant pressure), according to the author, the reciprocal relation is not to be regarded as necessary; that is, it cannot be generally concluded that k has the same value for every monatomic molecule. It is sufficient to assume that the energy of the rotatory movements represents a very small and negligible part of the progressive movements, and that no—or only very slight—movements take place between the several atoms within the molecule in order to justify the assumption that also in polyatomic gaseous molecules the value 1.67, or an approximate number, can be obtained for k . If, further, the value 40 were absolutely demonstrated as the atomic weight of argon, this element would find no place in the periodic system, and the system itself would be subverted; as would also be the case if a value were found for tellurium higher than that for iodine.

If we assume the value 20 for argon, it may find a place in the 8th group between fluorine and sodium. This place in the periodic system seems very suitable, especially as the transition from fluorine to sodium is not at all mediated. If, according to the conjecture of the discoverers, argon consists of two elements with the atomic weights 37 and 82, we could no longer admit the eighth group in the sense now admitted. It would then be necessary to assume the existence of a new element after each halogen, so that, e.g., an element of the atomic weight 20 would follow after fluorine, and another between iodine and cesium. These elements would then form an eighth group and conclude the period, whilst the present eighth group must form a new group—the ninth.

In the present position of the question we must abandon either the conclusions universally deduced from the kinetic theory of gases or the periodic system.

As long as more cogent evidences cannot be brought forward, the author does not believe that 40 represents the true atomic weight of argon.—*Gazz. Chim. Italiana* and *Chemiker Zeitung*.

ON THE DETERMINATION OF ARGON.

By TH. SCHLÆSING, Jun.

THE procedure for the determination of argon described in my last paper (*Comptes Rendus*, cxxi., No. 16; *CHEM. NEWS*, lxxii., p. 211) yields, according to the verifications submitted, results too low by an average of 0.6 per cent. This error is not great; we know its direction and we may accept it. I have sought to ascertain its cause, not so much in order to arrive at a closer approximation, as in the hope of detecting some reaction which is the origin of the slight loss observed.

In the apparatus which I have described, argon is brought in contact at a red heat with magnesium, copper, cupric oxide, steel, porcelain, and asbestos. Can it be some one of these substances which has a slight action

upon argon? In order to answer this question I have performed a methodical series of experiments, causing volumes of argon, accurately measured, to circulate in the apparatus for a certain time, then extracting them, and re-measuring them after having been submitted to the spark in presence of oxygen and potassa, the conditions of the experiment having been successively modified, so that we may perceive the influence of each.

These experiments, which it would be too tedious to describe in detail, have shown that the total of the somewhat complex manipulations of a determination involves a small loss of about 0.25 per cent of argon, when the magnesium tube has not been heated; that the total loss is between 0.5 and 1 per cent if the tube is heated as for an ordinary operation; that it increases slightly with the duration of the experiment, and also with the tension of the argon in the apparatus; and that it does not appear distinctly due either to the steel, the porcelain, the asbestos, the copper, or the cupric oxide. It followed already from the experiments of Lord Rayleigh and Prof. Ramsay that argon is not appreciably absorbed by copper or by cupric oxide, and here the fact is verified with all needful precision.

Among the experiments which I mention, those in which the tube of steel or of porcelain is heated, as in the majority of the determinations, for an entire hour have given the following losses:—0.70, 1.13, 0.66, 0.69, 0.63, 0.43, 0.51, or a mean of 0.68 per cent of the argon. This figure, 0.68 per cent, agrees well with that (0.62) of the experiments of verification referred to above. In fine, we may admit that for a series of determinations the mean error is approximately 0.7 per cent.

I have applied the procedure in question to the determination of argon in normal air. It has given the following results:—

Normal Air taken in Paris at about 10 metres above the Ground.

		ARGON	
		In 100 vols. of atmospheric nitrogen.	In 100 vols. air containing 79.04 of nitrogen.
Sept. 25		1.185	0.9369
" 26		1.183	0.9349
" 30		1.185	0.9367
Oct. 1		1.180	0.9325
" 4		1.185	0.9363
Mean..		1.184	0.935
		In 100 vols. of atmospheric nitrogen.	In 100 vols. of air.
Air taken in Normandy, on a hill of 305 metres high		1.182	0.9343
Air taken at 300 metres high on the Eiffel Tower		1.180	0.9328
Air taken in an iron mine		1.183	0.9354
Mean..		1.182	0.934

The slight respective differences shown by these results are of the rank of experimental errors. They do not necessarily correspond with real variations of the amount of argon in the air. If such variations occur they are probably very slight. Thus it must be laid down for argon as for the two most abundant elements of the atmosphere, oxygen and nitrogen, its proportion varies only to a degree scarcely perceptible on analysis. The constant composition of our atmosphere is explained, as it is known by the incessant stirring to which it is submitted. As regards argon, its chemical inactivity, if confirmed, would be another reason why it should not vary.

If we make the correction of 0.7 per cent in addition to the above means as regards normal air they become 1.192 and 0.941. We may easily calculate the difference with this figure of 1.19 per cent (the first cause of the discovery

of argon) between the weight per litre of atmospheric nitrogen and that of chemical nitrogen—a difference which Lord Rayleigh and Professor Ramsay determined directly by measurements of great precision, and found equal to 1.2572 grm.—1.2505 grm., or 0.0067 grm. If, in fact, D_1 , D_2 , and D_3 are respectively the weights per litre of argon, of chemical nitrogen, and of atmospheric nitrogen we should have—

$$0.0119 D_1 + (1 - 0.0119) D_2 = D_3,$$

whence—

$$D_3 - D_2 = 0.0119 (D_1 - D_2).$$

Now, the experiments of Rayleigh and Ramsay show us D_1 and D_2 . They have given $D_2 = 1.2505$ grm., and for the density of argon with reference to hydrogen 19.9, or for the weight per litre 19.9×0.0896 grm., or 0.783 grm. We have, therefore, with a sufficient precision $D_1 - D_2 = 0.5325$ grm. and $D_3 - D_2 = 0.0063$ grm. This value of 0.0063 grm. of the difference in question ought to be, in consequence of the procedure by which it is obtained, a closer approximation than the foregoing 0.0067 grm.

Here follow some results referring to gases extracted from agricultural soils.

	Argon for 100 vols. of nitrogen accompanied with argon.
Gas taken at a depth of 0.20 metre in the soil of a pine forest	1.170
Gas taken at a depth of 0.40 in a ploughed soil.	1.169
Gas taken at a depth of 0.40 in a ploughed soil.	1.155
Gas taken at a depth of 0.40 in the soil of a garden	1.118

The mean of these figures is lower than that corresponding to normal air, which depends in part on the solvent action of water (argon, according to Rayleigh and Ramsay, about $2\frac{1}{2}$ times more soluble in water than is nitrogen), always supposing that the rain reaches the soil before it has taken up from the air all the proportion of argon which it can dissolve.—*Comptes Rendus*, cxxi., p. 604.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 241).

D. On the Holders used to hold Compounds in an Electric Spark or Discharge.—To hold the compounds to be volatilised I used platinum or iridium balls 3 m.m. in diameter, at the end of a platinum wire 1 m.m. in diameter, or, better still, small cones of purified carbon fixed to a platinum wire. The platinum or iridium balls, and the small carbon cones, were completely covered with the compounds in the form of anhydrides or hydrates, or sometimes merely soaked in a saturated solution of the compound to be volatilised.

I made different arrangements according as I passed the spark or current in the surrounding air, or in purified air, or in pure hydrogen.

When I worked in the outer air I clamped, and held by screw clips, the platinum wires, ending in balls or small carbon cones covered with the compounds, between two separate and insulated metal rings. The two metal rings were attached to a varnished glass stem by means of insulated supports. The glass stem was mounted on a metal stand; it could be raised or lowered by means of a rack with which the stand was furnished. Thanks to these arrangements, one could raise to any height required the two rings attached to the stem, adjust the distance

between the balls or saturated carbon cones, and pass the spark or discharge between them.

Having arranged the apparatus in front of, and as near as possible to, the slit of the spectroscopic, and having guarded it against spattering by interposing a thin sheet of mica, one can at will let through the slit of the spectroscopic the rays from either the middle of the spark or from either of its ends.

When the platinum balls or the carbon cones were completely covered by the compounds to be volatilised, spectrum analysis of a spark, or even a discharge, showed no lines due to platinum or carbon.

When working in purified air, or, better still, in pure hydrogen, I used the same platinum wire holders, ending in balls of this metal or of iridium, or carbon cones, completely covered with the compounds to be volatilised in the spark or discharge; but in this case I arranged the platinum wires by means of well-washed corks in a glass tube open at both ends, from 2 to 3 c.m. diameter by 10 c.m. in length.

At a distance of 2 c.m. from each end was fixed a small glass tube, furnished with a cock meant to admit and maintain a current of purified air or pure hydrogen whilst the sparks or electric discharges were passing.

Whatever care might be used in fitting the apparatus, it was impossible to prevent the outer air from diffusing into the gas in the tube, especially when this gas was hydrogen. For this reason it was necessary to maintain the current during the experiment, and at least to completely cover the corks fitted to the tube, as well as a part of the tube itself, with a layer of melted shellac or wax.

When working with a spark in the open air I sometimes did and sometimes did not see atmospheric lines. In a note* I give the reason of the appearance and disappearance of atmospheric lines.

Spectrum analysis of the discharge in air enabled me to detect the constant presence of atmospheric lines superposed on the lines of the compound volatilised in the discharge. This constant presence makes observations of a discharge painful and uncertain.

Passing a short spark in hydrogen showed only the red hydrogen line with the spectrum of the volatilised compound, whilst a discharge in hydrogen constantly shows the red and bluish green C and F lines superposed on the spectrum of the volatilised compound, the F line appearing as a band shaded on both sides. However intense the discharge might be, I could not detect the other hydrogen lines.

To put a saline solution into an electric spark or discharge, I took a clear glass tube, open at both ends, 10 c.m. long by 3 c.m. diameter, fitted with glass taps in the sides, towards the top and bottom, to admit a current of pure air or hydrogen. In the lower end of the tube I fitted a plug of pure rubber, very slightly tapered, pierced by a platinum rod 3 m.m. diameter, terminating above in a tripod of the same metal, and having a hole below to make contact with the positive electrode.

I placed on the tripod a platinum dish slightly smaller than the diameter of the tube, containing a hollowed cone of this metal with a capillary hole through it, the top of which was about 2 m.m. above the top of the dish. I filled this dish with the saline solution to be put in a spark or discharge which flashed from the liquid covering the top of the cone.

The upper end of the tube was fitted with a slightly tapered plug of pure rubber, pierced by a pure platinum rod 3 m.m. diameter, terminating below in a point, and with a hole above to make contact with the negative electrode.

Before receiving the saline solution to be put into the electric spark or discharge, the dish as well as the platinum cone held in it were washed with very dilute hydrochloric acid, then with pure water, and finally made white-hot.

* CHEMICAL NEWS, vol. lxxii., p. 226 (and footnote).

The terminal point of the platinum rod, before being adjusted vertically above, and from 2 to 3 m.m. from the top of the platinum cone, was treated in the same way as the dish.

Thanks to the pure rubber plug, this apparatus preserved perfectly the pure air and hydrogen contained in it. When working in air, the liquid, being in contact with platinum *only*, yielded, on spectrum analysis of the spark saturated with the liquid which rose by capillarity to the top of the cone, the spectrum proper to the compound, to which nevertheless was often added the red hydrogen line. Spectrum analysis of a spark showed the same spectrum, to which was added some atmospheric lines. When passing a spark or discharge in hydrogen, one saw the spectrum of the saline liquid, to which was added either the red hydrogen line or the reddish and the bluish green, or more frequently greenish blue, hydrogen lines.

When one substitutes, as is generally done, for the apparatus arranged as described above, a glass tube which is itself used to hold the saline solution, and when one prolongs for some time the sparks, and, better still, the discharge, one notices that the spectrum seen shows the sodium D line and some calcium lines, even though the saline solution in the tube contains *neither sodium nor calcium*. As a matter of fact, in the apparatus usually used, the calcium and sodium are obtained from the glass by the attack on the tubes near the platinum wires, and especially on the small glass cone, which admits the wire used for the positive electrode.

When using apparatus of which all parts to be put in contact with a saline solution are made of platinum, the method of analysing a spark or discharge saturated with a saline solution shows an advantage over the analysis of a spark or discharge passed between balls or cones coated with solid compounds, whether anhydrous or hydrated. In fact, in the former apparatus, one can make the compounds with which one wishes to saturate the spark or discharge, in a close tube filled with air or hydrogen. Relying on this possibility I tried to ascertain whether one could get, by means of calcium oxide, hydrochloric acid, or nitric acid, *free from sodium*, some dissolved chloride or nitrate of calcium, which, when introduced into a spark or discharge, would not show the sodium line on spectrum analysis, a thing I could not accomplish with compounds made in the open air. I showed this possibility, and I satisfied myself *absolutely* that the presence of sodium in a chloride or nitrate prepared in the open air is due to the sodium contained in the air. In the notes on the flame and electric spectra of chloride and nitrate of calcium I describe my observations on this point.

The method of experimenting described above has a fault which I ought to mention. It is, in many instances, a fact that spectrum analysis of a spark or discharge, in a strong or weak, neutral or acid, solution of any of the metallic compounds, fails to show always a spectrum containing *all the characteristic lines of these compounds*.

In many cases the spectrum is incomplete. Thus, whatever spectroscope be used, spectrum analysis of a spark through a sodium salt only shows *one-third* of the lines seen in the electric spectrum of sodium salts.

Experience has taught me that the greater or less volatility of the compounds is not the reason of the appearance of complete or incomplete spectra; for a spark, which only shows one-third of the lines in the electric spectrum of sodium, shows a barium spectrum identical with that of an electric arc saturated with barium.

According to my experience and the checks to which I have submitted my researches, in collaboration with M. Depaire, this method of spectroscopic research, whatever services it may have yielded, is not competent to give a decisive indication as to the *presence or absence* of a given body in a compound submitted to analysis.

E. On the Holders used to Volatilise Different Bodies in an Electric Arc.—To volatilise the different bodies in which I was carrying on my investigations in an electric

arc, I first acted in the same way as when placing the same bodies in an electric spark or discharge,—that is to say, I used rods of pure carbon, of considerable length and diameter, with their extreme ends covered with these bodies, just as I have already described in notes on my studies of different metals and metallic compounds. But I soon learnt the weak points, or I might even say the errors of principle, which are associated with this method of experimenting. The voltaic current being established by connecting the poles and the volatilising of the compounds which covered them, the poles were brought at once to the brightest incandescence. This incandescence was less or greater according as the electrodes were in contact or were separated to make an electric arc. The sum of the light from the poles and from the electric arc proper are said to form the *electric light*.

But in his researches "On the Temperature of the Carbon Poles at the Instant they make the Electric Light, and on the Temperature of the Electric Arc," Rossetti found, at the end of the *positive* pole, a maximum temperature of 3900°, at the end of the *negative* pole a temperature of about 3750°, and in the arc itself a temperature of 4800°, whatever might be the diameter of the arc and the intensity of the current which produced it.

Besides, when looking closely into an arc which passes between two poles, one sees at once that its structure is not simple. At the beginning—that is to say, in the *crater* whence the arc springs—it emits sky blue rays. The arc proper is of a purplish blue colour. This difference of colour between the arc at its origin and the body of it shows it to be surrounded by a pink-red gaseous envelope, of which the colour deepens gradually from the outside of the arc towards the *sky-blue* part.

The arc, at its origin, appears to me to consist of carbon vapour, whilst the centre is composed of the same current of carbon vapour, but partially oxidised by its contact with the air which flows continually round the arc. The colour of the envelope of the arc closely resembles the tint which the inner cone of an oxyhydrogen blowpipe assumes when one puts a filament of pure carbon into it. Since an oxyhydrogen blowpipe supplies a considerable excess of hydrogen mingled with oxygen, the carbon burns in it with the greatest brilliancy, and the flame produced thus is either red or pink, according as one looks at it near the point where the filament is held in the blowpipe, or at a part distant from that point. I have seen the same pink-red colour when distilling silver contained in a pure carbon retort in an oxyhydrogen or oxy-coal-gas blowpipe. The flame which issues from the retort is pink-red, in spite of the large quantity of silver vapour it contains.

The temperature of the gaseous envelope surrounding the arc is excessive. It greatly exceeds the fusing-point of pure platinum, which is that of the inner cone of an oxyhydrogen flame. In fact, pure iridium attached to a carbon filament melts rapidly when put into it.

Pure iridium which one drops into the *crater* of an arc *two and a half c.m.* long, with a carbon spatula, is volatilised at once, and in a very short time covers the negative pole with small drops of melted iridium.

The poles emit *heat* rays; the arc emits both *electric* and *heat* rays; as determined in my researches on the heat and electric spectra of sodium in an electric arc. When one projects into the slit of a spectroscope, a beam of parallel rays from the poles and the arc at once, and saturates the arc with a volatilised compound which has a *different* heat and electric spectrum, the image has the characteristic lines of both spectra.

It follows from these facts that, when using an electric arc to study the spectrum of a body, one ought to throw parallel rays coming from the poles, and parallel rays coming from the arc, *separately* on the slit of the spectro-

scope, as I have taken care to do since I have understood the complexity of the electric light.

(To be continued).

ON THE VAPOUR-TENSIONS OF MIXTURES OF VOLATILE LIQUIDS.*

By C. E. LINEBARGER.

(Continued from p. 239).

Vapour-tensions of Mixtures of Acetic Acid with Benzene and with Toluene.

Two series of determinations were carried out on the mixtures of benzene and acetic acid, one at 35° and one at 20°, but one, however, for the mixtures of toluene and acetic acid, at 35°. In order to apply to the experimental results of the work our mode of calculation of the vapour-tensions, it is necessary to know the molecular mass of gaseous acetic acid at the above two temperatures.

* Abridged from the *Journal of the American Chemical Society*, vol. xvii., No. 8, August, 1895.

Now acetic acid even in the vaporous condition is made up in part of polymerised molecules, so that it is not legitimate to set its molecular mass equal to that corresponding to the formula $C_2H_4O_2$. What the actual molecular mass of the gaseous acid at 35° and 20° is can be easily calculated by the aid of the vapour-density determinations of Bineau ("Recherches sur les Relations des Densités des Vapeur avec les Equivalents Chimiques;" *Ann. Chim. Phys.*, xviii., 226, 1846), which are the more applicable to the case in hand as his vapour-density measurements were made under the same conditions as my vapour-tension determinations; that is to say, Bineau measured the amount of acetic acid that diffused into a definite volume of air at a fixed temperature. The molecular mass of acetic acid as deduced from Bineau's observations is 104 for 35° and 110 for 20°. It may be worth while to remark that an error of five in the molecular mass will not entail an error of 1 millimetre in the vapour-tension; we may with all confidence then adopt the above molecular masses of acetic acid in state of vapour as quite accurate.

The necessary data of the experiments are given in Tables X. to XII.; the superscription to each vertical column renders any explanation of them here superfluous.

TABLE X.—Vapour-Tensions of Mixtures of Benzene and Acetic Acid at 35°.

Vapour-tension of Benzene at 35° is 146 m.m. of Mercury.

Vapour-tension of Acetic Acid at 35° is 26.5 m.m. of Mercury.

P.c. of $C_2H_4O_2$ in liquid mixt.	P.c. of $C_2H_4O_2$ in gaseous mixt.	Grms. $C_2H_4O_2$ in vapour.	Grms. C_6H_6 in vapour.	Tension of $C_2H_4O_2$ in m.m.	Tension of C_6H_6 in m.m.	Volume of air in m.m.	Barometer in m.m.	Internal pres. m.m.
6.44	2.45	0.0461	1.3759	3.5	140.0	1955	758	14
15.17	4.74	0.0834	1.3580	6.4	129.2	1958	758	15
37.10	8.25	0.0700	1.5840	10.5	117.0	1020	767	16
43.99	11.02	0.0867	0.5243	13.2	106.5	1019	766	16
49.86	12.26	0.0931	0.4849	14.0	103.1	1020	766	17
53.24	13.33	0.0969	0.4731	14.9	97.6	1020	766	17
54.65	13.82	0.0990	0.4630	15.3	97.3	1020	766	17
56.60	14.62	0.1063	0.4677	16.4	96.0	1020	766	17
73.87	20.18	0.1156	0.4585	18.4	72.7	1019	766	16
80.00	26.91	0.1351	0.2751	22.3	59.3	1020	766	17

TABLE XI.—Vapour-Tensions of Mixtures of Benzene and Acetic Acid at 20°.

Vapour-tension of Benzene at 20° is 75.6 m.m. of Mercury.

Vapour-tension of Acetic Acid at 20° is 11.7 m.m. of Mercury.

P.c. of $C_2H_4O_2$ in liquid mixt.	P.c. of $C_2H_4O_2$ in gaseous mixt.	Grms. $C_2H_4O_2$ in vapour.	Grms. C_6H_6 in vapour.	Tension of $C_2H_4O_2$ in m.m.	Tension of C_6H_6 in m.m.	Volume of air in c.c.	Barometer in m.m.	Internal pres. m.m.
53.24	11.99	0.0440	0.2291	6.6	48.7	1018	760	16
80.00	21.97	0.0576	0.2100	9.1	33.0	1018	760	16
97.28	64.66	0.0674	0.0276	11.4	6.2	1018	760	16

TABLE XII.—Vapour-Tensions of Mixtures of Toluene and Acetic Acid at 35°.

Vapour-tension of Toluene at 35° is 47.2 m.m. of Mercury.

Vapour-tension of Acetic Acid at 35° is 26.5 m.m. of Mercury.

P.c. of $C_2H_4O_2$ in liquid mixt.	P.c. of $C_2H_4O_2$ in gaseous mixt.	Grms. $C_2H_4O_2$ in vapour.	Grms. C_7H_8 in vapour.	Tension of $C_2H_4O_2$ in m.m.	Tension of C_7H_8 in m.m.	Volume of air in c.c.	Barometer in m.m.	Internal pres. m.m.
49.00	32.66	0.0911	0.1661	15.0	31.8	1020	760	18
60.88	37.91	0.1025	0.1485	17.4	28.5	1020	760	18
83.37	56.36	0.1252	0.0858	22.2	16.7	1020	760	18

TABLE XIII.—Partial Pressures of Benzene, Acetic Acid, and Toluene.

Per cent of $C_2H_4O_2$ in liquid mixture.	Partial pressure of $C_2H_4O_2$ at 35° in m.m.	Partial pressure of $C_2H_4O_2$ at 35° in m.m.	Partial pressure of C_7H_8 at 35° in m.m.	Partial pressure of C_6H_6 at 20° in m.m.	Partial pressure of $C_2H_4O_2$ at 20° in m.m.
10	138.4	2.8	44.5	71.4	1.2
20	130.9	5.6	41.6	67.5	2.3
30	122.2	8.2	38.6	63.1	3.5
40	112.6	11.1	35.0	58.2	4.8
50	102.4	13.6	31.9	53.2	6.0
60	90.7	16.2	27.8	47.1	7.2
70	76.7	19.1	23.1	40.1	8.4
80	59.1	21.7	18.4	31.1	9.6
90	35.1	24.2	11.1	18.5	10.7

From these data curves were constructed on a large scale with percentages of composition as abscissæ and vapour-tensions as ordinates (1 inch on the axis of abscissæ corresponded to 5 per cent; 1 inch on axis of ordinates to 10 m.m. of pressure); these proved to be perfectly regular, and passed directly through most of the points.

The points for acetic acid either fell upon or very close to the straight line connecting the left hand origin of the co-ordinate system with the point on the right hand axis of ordinates corresponding to the value of the vapour-tension of pure acetic acid at the temperature in question, viz., 26.5 for 35°, and 11.7 for 20°, the acetic acid vapour-tension curve is simply a straight line, then, when the composition is expressed in percentages. An interesting conclusion to be drawn from this fact is that the partial tension of acetic acid is the same, be it mixed with benzene or with toluene; the specific influence of the diluting liquid seems to be extremely slight, if, indeed, there is any at all. This circumstance also indicates that the molecular condition of the acid is the same when it is dissolved in either of the hydrocarbons so as to form solutions of the same strength; this insight into the molecular structure of acetic acid enables us to determine by a little calculation its molecular mass not only in the dissolved but also in the pure state. In the following section will be set forth the *modus operandi*.

From the curves drawn as just described above, the partial pressures of the various constituents of the mixtures were taken for concentrations corresponding to 10, 20, 30, . . . 90 per cent of acetic acid; the data thus obtained are given in Table XIII.

(To be continued)

THE QUANTITATIVE DETERMINATION OF PERCHLORATES.*

By D. ALBERT KREIDER.

(Continued from p. 242).

THE results obtained by substituting (a) cadmium iodide and (b) anhydrous zinc chloride for the double chloride of aluminium and sodium are recorded in Table VI. In (27), (28) and (29) cadmium iodide was used, and the iodine obtained by treating the cooled mass with dilute sulphuric acid (1 : 6) and potassium iodide for the reduction of cadmium oxide in each case added to that of the receivers. In (30) and (31) zinc chloride was employed, but no additional iodine was obtained by treatment with sulphuric acid and potassium iodide.

TABLE VI.

KClO ₄ taken.	KClO ₄ found.	Error.
Grm.	Grm.	Grm.
(27) 0.1000	0.0745	0.0255—
(28) 0.1000	0.0693	0.0307—
(29) 0.1000	0.0679	0.0321—
(30) 0.1000	0.0245	0.0755—
(31) 0.1653	0.1156	0.0497—

In (31) manganous chloride was mixed with the zinc chloride in the proportion of 2 : 1, in the hope of strengthening the reducing action. The black colour of the fusion revealed the formation of manganese dioxide, the equivalent of which in iodine was obtained by dissolving the cooled mass in water, adding dilute sulphuric acid and a known amount of ammonium oxalate, titrating the residual oxalate with permanganate solution, and calculating the difference into iodine, which was added to that obtained by titrating the contents of the receivers. This addition of manganous chloride to the fusion of the double chloride of aluminium and sodium was forestalled

by the necessity of subsequent solution of the fused mass, which contained an impurity in the form of ferric chloride, which of course in the presence of hydriodic acid would be reduced with evolution of iodine.

It was evident from all these results, as well as those obtained by use of other salts not necessary here to record, that fusion with salts of the halogens would not suffice for the complete reduction of perchlorates, or at least would not quantitatively register the result in the halogen liberated. The well-known reaction of the oxidation of chromic oxide by fusion with alkaline carbonates was also applied. A combustion-tube was used for the fusion, sealed at one end, and, after the insertion of chromic oxide with a mixture of sodium and potassium carbonate, restricted at the other end so as to admit a small tube by which carbon dioxide could be entered to expel all air. A blank determination gave no chromate. When 0.1 grm. potassium perchlorate was mixed with an excess of chromic oxide and alkaline carbonate, and carefully fused from the top, and kept in a state of fusion throughout its length in an atmosphere of carbon dioxide, the fusion subsequently dissolved in water, and the chromic oxide removed by filtration, an amount of chromate was obtained on titration equivalent to only 0.0347 grm. of potassium perchlorate.

Powerful as were the various reducing agents employed for the decomposition of perchlorates, they were all successfully resisted, even at the highest permissible temperatures; and if anything is proved by the results of the experiments above recorded, it is that perchloric acid is, in combination, one of the most powerful and stable acids known. Certainly nothing short of high temperatures is capable of overcoming the remarkable affinity by which the oxygen of this acid is held by its salts. At about 400° C. the potassium salt fuses with evolution of oxygen, and as a last resort an attempt was made to have the oxygen thus obtained act on hydriodic acid by intervention of nitric oxide. It was the application of this principle that led to the final method, which, both as to manipulation and results, leaves nothing to be desired.

The method is essentially the collection of the oxygen of the perchlorate; its subsequent passage into an atmosphere of nitric oxide over a strong solution of hydriodic acid, and the titration of the iodine thus liberated with decinormal arsenic in alkaline solution. The apparatus employed consisted of a piece of combustion tubing 10 or 12 c.m. in length, drawn out at one end to a narrow restriction of length sufficient to prevent the action of the heat on the rubber tubing connecting it with a receiver filled with caustic potash. The tube must of course be cleansed from all organic materials, and cannot be safely employed for more than three fusions. A platinum boat (porcelain fusing to the glass) served for the introduction of the perchlorate to the combustion-tube, and, in order to bring about a gradual and quiet fusion, the perchlorate was covered with a small amount of an equal mixture of dry and pure sodium and potassium carbonates. Carbon dioxide obtained from a Kipp generator, the acid and marble of which had been previously boiled to expel all traces of air, and to which a little cuprous chloride had been added to take up any oxygen which might be absorbed from the top, was passed through a solution of iodine in potassium iodide to remove a trace of reducing agent which it was found to contain, and then washed with potassium iodide solution before being used. The larger end of the combustion-tube was closed with a perforated rubber stopper by which it was attached to the carbon dioxide apparatus. After all air had been expelled from the inclined tube by means of carbon dioxide, it was connected by a short glass capillary and vacuum tubing joints with the receiver, into which about 50 to 100 c.m.³ of gas was allowed to flow before the combustion was started, and thus, when only a small but inevitable bubble remained insoluble in the caustic potash, the complete removal of air was indicated. To prevent the caustic potash from drawing into the combustion-tube, a little

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. 1., October, 1895.

more carbon dioxide was entered, when the current was closed by a pinchcock on the side towards the generator, and heat gradually applied—with perforated asbestos cards on either side to check its radiation to the rubber—and continued till the contents of the platinum boat was in a quiet state of fusion. By lowering one of the bulbs of the caustic potash receiver, the oxygen was evolved under slightly diminished pressure, and thus the chances of less decreased. Then the tube was again inclined and carefully annealed, while a current of carbon dioxide carried all of the oxygen into the receiver, which was then closed and disconnected. As a receiver, two levelling bottles were found vastly superior to a burette, the glass stopcocks of the latter giving continual trouble by the action of the caustic potash upon them. I found that gas could be removed from a levelling bottle without the loss of a particle, if a perforated rubber stopper containing a capillary tube, which reached just even with the narrower end, was by a slight twist forced tightly into the neck of the bottle. In this way a regular funnel-shape was obtained, and the oxygen could be withdrawn without the slightest bubble remaining. The other end of the capillary was fitted with a short piece of vacuum tubing and screw pinchcock, which worked incomparably better than the glass stopcocks. The larger capacity of the bottle was favourable for the volume of oxygen evolved, and its shape offered superior facilities for the absorption of carbon dioxide.

For the action of the oxygen on hydriodic acid through the medium of nitric oxide, various devices were tested. Passing it directly into nitric oxide over a solution of hydriodic acid in a Hempel absorption bulb was found to yield low and irregular results, due doubtless to the formation of nitric acid wherever the nitrogen trioxide or peroxide, as the case might be, met water in which the hydriodic acid had been exhausted,—as, for instance, along the sides of the bulb. Shaking the bulb as the oxygen entered improved the action, but was not sufficient. It was evident that, for a complete action, the hydriodic acid solution must be strong and on the spot where the higher oxide of nitrogen is formed; and to avoid excessive use of the iodide the volume of water must be kept at a minimum. Letting a solution of hydriodic acid saturated with nitric oxide flow slowly into the Hempel bulb in which the oxygen was contained over water, was so slow in its action that a quantitative test was not applied. The plan of mixing the two gases under a strong solution of hydriodic acid by means of two capillaries with adjoining openings, was more effective and rapid, but it was wasteful of nitric oxide, which for complete action would have to flow in continual excess, whereas only a small amount of nitric oxide would really be necessary for the reaction, since it could be used and re-used for the transfer of free oxygen to the hydriodic acid. A simple piece of apparatus was then devised to meet all these conditions. It consisted of a 100 c.m.³ bulb pipette, cut off short at either ends with stopcocks sealed to both stubs. The delivery-tube of one of the stopcocks was cut off rather short after being tapered and restricted so as to hold a rubber connector tightly, while the other delivery-tube was left long enough to reach to the bottom of an Erlenmeyer beaker. It is a convenience to have these conducting tubes 3 or 4 m.m. in diameter rather than capillaries, since for the various connections all air may be expelled from them by displacement with water, which is easily accomplished by using a long-nozzled wash-bottle. By attaching the shorter end to an ordinary water-pump the air was partially exhausted, when the stopcock was closed, and the bulb disconnected and lowered into a solution of hydriodic acid of approximately known strength, obtained by acidifying potassium iodide with hydrochloric acid. When the desired amount of liquid had been drawn in, the stopcock was closed and connection made with the carbon dioxide, by which all residual air was expelled. Then the bulb, held so as to prevent the escape of the liquid, was again exhausted by

attachment to the pump. After about 10 c.m.³ of nitric oxide were admitted, attachment was made to the receiver containing the oxygen, which was allowed to enter slowly under the diminished pressure within the bulb, and with continuous shaking of the contents of the latter. The latter precaution is essential to the process, as otherwise there is imperfect distribution of the hydriodic acid and the danger of forming nitric acid. But when the solution of hydriodic acid is kept strong, and the shaking continued while the oxygen enters and for a minute or two afterward, depending on the rapidity with which it was admitted, the oxygen may be allowed to enter quite rapidly without any fear of imperfect action. The oxygen being immediately utilised, the partial vacuum is effected only by the heat generated, which is scarcely noticeable. As a rule, the bulb and contents were well cooled before the oxygen was admitted.

(To be continued).

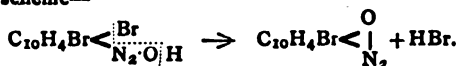
PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

THE following are the abstracts of papers received during the vacation, and published in the *Transactions*:—

104. "*Homonuclear Tri-derivatives of Naphthalene.*" By RAPHAEL MELDOLA, F.R.S., and FREDERICK WILLIAM STREATFEILD.

Dibromonitronaphthalene, $C_{10}H_6Br_2NO_2$ (1 : 2 : 4), m. p. 117° , has been prepared by the authors and submitted to further study. The corresponding dibromo- β -naphthylamine consists of white silky needles melting at $106-107^\circ$; the acetyl-derivative melts at $220-221^\circ$. When this dibromo- β -naphthylamine is diazotised in the presence of an excess of mineral acid and the diazo-salt solution boiled with water, the NH_2 -group is not replaced by hydroxyl, as in the normal Griess reaction, but bromine is displaced, and a diazoxide formed in accordance with the scheme—



The diazoxide has the constitution $O : N_2 : Br = 1 : 2 : 4$. It consists of ochreous needles, soluble in boiling water, and decomposing at $148-151^\circ$. It is reduced by tin and hydrochloric acid to β -amido- α -naphthol, and bromine and glacial acetic acid converts it into dibromo- α -naphthoquinone, m. p. 216° .

Chlorobromo- β -naphthylamine, $C_{10}H_6ClNH_2Br$ (1 : 2 : 4), was obtained in the form of white silky needles melting at $102-103^\circ$; the acetyl derivative at 218° , the benzoyl derivative at $185-186^\circ$. By nitrous acid this chlorobromo- β -naphthylamine is converted into the diazoxide, above described, in the presence of excess of mineral acid; in its absence the diazoamide, $C_{10}H_6ClBrN_2NH \cdot C_{10}H_5ClBr$, is formed. This compound is very stable for a diazoamido-compound, and crystallises from toluene in yellowish needles melting at $205-210^\circ$, with decomposition. The authors also show that iodine chloride is an excellent reagent for preparing iodine derivatives of the acetnaphthalides, both α and β . They give the melting-points of the following compounds:— $C_{10}H_6I \cdot NHAc$ (4 : 1), 197° ; $C_{10}H_5NO_2 \cdot I \cdot NHAc$ (2 : 4 : 1); $C_{10}H_5NO_2 \cdot I \cdot OH$ (2 : 4 : 1), 150° (shrinking at 147°); $C_{10}H_5NO_2 \cdot I \cdot OC_2H_5$ (2 : 4), $104-105^\circ$. The potassium salt of the nitroiodonaphthol has also been prepared and analysed.

105. "*The Ethereal Salts of the Optically Active Lactic Chloropropionic, and Bromopropionic Acids.*" By J. WALLACE WALKER, M.A.

The methylic, ethylic, and propylic ethereal salts of

active lactic acid were prepared by the action of the alkyl iodides on the anhydrous silver salt. From the ethereal lactates the corresponding bromopropionic salts were prepared by the action of phosphorus pentabromide. For both series of salts there is a constant difference in rotatory power, in the first case of 5.5° , in the second of 14.2° , between two adjacent members. The ethereal chloropropionates were prepared by the action of phosphorus pentachloride on lactic acid. These bodies possess a high degree of optical activity, and the values given in this paper are much higher than those found by Le Bel, Walden, and Frankland and Henderson for such of the substances as they have examined. The observed results do not agree with Guye's hypothesis.

106. "Some New Azo-compounds." By CHARLES MILLS.

By the action of nitrosobenzene on aniline dissolved in acetic acid azobenzene is produced (Baeyer, *Ber.*, vii., 1638). The author has extended this reaction, and has prepared the following substances:—

m-Acetylaminodiazobenzene, m. p. $130-131^\circ$ C. On hydrolysis with caustic soda it gives *m*-amidoazobenzene, crystallising from light petroleum spirit in long, silky, orange needles, m. p. $56-57^\circ$ C. Readily soluble in alcohol, acetic acid, ethyl acetate, acetone, chloroform, benzene, and ether. $C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_5$, *di*-*para*-diphenyldiazophenylene, prepared by the action of nitrosobenzene on *p*-amidoazobenzene. *p*-Benzeneazotoluene formed by the action of nitrosobenzene on *p*-toluidine, also by the action of *p*-nitrosotoluene on aniline.

The following compounds are also described:—*p*-Benzeneazotoluenesulphonic Chloride. *p*-Benzeneazotoluene, $C_6H_5 \cdot CH_2 \cdot NHAc \cdot N \cdot N \cdot C_6H_5$ (1 : 2 : 4). *m*-Amido *p*-benzeneazotoluene. Benzene-*o*-*azo*-*o*-acetylulide, $C_6H_4 \cdot NHAc \cdot CH_2 \cdot N \cdot N \cdot C_6H_5$ (1 : 2 : 3). *m*-Amido-benzene-*o*-azotoluene, $C_6H_4 \cdot NH_2 \cdot CH_2 \cdot N_2 \cdot C_6H_5$ (1 : 2 : 3).

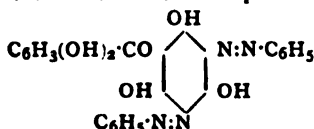
107. "Some Derivatives of Maclurin." By C. S. BEDFORD and A. G. PERKIN.

When an aqueous extract of old fustic (*Morus tinctoria*) is treated with a solution of diazobenzene sulphate, a colouring-matter is produced. The chief constituents of old fustic are, morin, $C_{15}H_{10}O_7$, and maclurin, $C_{15}H_{10}O_6$, only the latter reacts readily with diazobenzene. Benzeneazomaclurin,—



o- and *p*-tolueneazomaclurin, *p*-nitrobenzeneazomaclurin, and maclurinazobenzene-*p*-sulphonate of sodium have also been prepared. These substances dye wool and silk orange-coloured to deep brown shades. Maclurin, by the action of reducing agents, yields phloroglucin and protocatechuic acid, and is considered to be a pentahydroxybenzophenone, $C_6H_3(OH)_2 \cdot CO \cdot C_6H_2(OH)_3$.

Phloroglucin combines with 2 mol. props. of diazobenzene, while no reaction takes place between this latter and protocatechuic acid. The constitution of benzeneazomaclurin should therefore be thus represented,—



108. "The Constituents of 'Artocarpus integrifolia.'" By A. G. PERKIN and F. COPE.

Artocarpus integrifolia is the well-known Jack Fruit, cultivated in India, Burmah, and Ceylon. It is much esteemed for carpentry, and is used in conjunction with alum as a yellow dye. It contains a yellow colouring matter of the formula $C_{15}H_{10}O_7$, identical with morin, and a substance of the formula $C_{15}H_{10}O_6$, to which the name cyanomaclurin has been given. With diazobenzene it yields a compound, $C_{15}H_{10}O_6(C_6H_5 \cdot N_2)_2$, crystallising in scarlet needles, which dyes unmordanted wool and silk orange to orange-red shades, but which does not dye with

mordants. When boiled with dilute acids, cyanomaclurin yields red-brown products, resembling in character the so-called "anhydrides" of catechin, which can be produced from this latter substance in a similar way. That first formed dissolves in hot water and dilute alkalis, but by longer treatment becomes more sparingly soluble, and the final product obtained is insoluble in dilute alkalis and the usual solvents. No glucose is produced during this reaction, so that cyanomaclurin is not a glucoside. The study of this substance will be continued.

109. "Optically Active Methoxy- and Propoxy-succinic Acids." By T. PURDIE, F.R.S., and H. W. BOLAM, B.Sc.

The authors have resolved inactive methoxy- and propoxy-succinic acids into their active components, the cinchonine and strychnine salts being made use of in the case of methoxysuccinic acid, the strychnine salts in the case of the propoxysuccinic acid.

Rotations of the acids in water and different organic solvents are given, with the rotations of salts of both acids in aqueous solution.

110. "Ethereal Salts of Active Methoxy- and Ethoxy-Succinic Acids." By T. PURDIE, F.R.S., and S. WILLIAMSON, Ph.D.

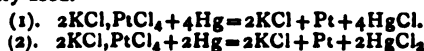
Inactive methoxy- and ethoxy-succinic acids were resolved into their active components by means of their strychnine salts. Observations on the activity of the various strychnine salts in aqueous solution were made, and results obtained in accordance with the law of Oudemans.

Methyl-, ethyl-, propyl-, and butyl-, methoxy-, and ethoxy-succinates, and the isopropyl and isobutyl salts of ethoxysuccinic acid, were prepared by the action of their respective iodides upon the silver salts of the acids, and their rotations observed.

The specific rotations of the active acids in water and various organic solvents were also taken. A discussion of the results obtained is contained in the paper.

111. "Note on the Production of Potassium Platinochloride." By E. SOMSTADT.

Dry potassium platinochloride, when heated with mercury, is decomposed according to the proportion of mercury used.



The decomposition begins even below 100° C., and is complete at a lower temperature than is required to expel from the containing vessel the mercurous or mercuric chloride produced.

In treating small quantities of the platinochloride, the mercury is placed in a porcelain crucible, and covered with platinochloride, in the proportion of about two parts of mercury to one of salt. Heat is applied very gently, to avoid loss through boiling, till the reaction is complete, when the heat is raised to expel the mercurous chloride.

When larger quantities are decomposed, the salt is preferably triturated with the mercury, and gently heated, so as to avoid a too sudden or violent reaction.

Additional Note by Author.—Dry silver chloride is not decomposed by mercury, even at a red heat; nor when mixed or combined with a platinum salt.

112. "Orthobenzoic Sulphinide." By WILLIAM J. POPE.

The author finds that pure orthobenzoic sulphinide in large well-defined crystals may be obtained from the commercial mixture known as "saccharin," by crystallisation from acetone. Crystallographical measurements are given.

113. "Derivatives of β -Resorcylic Acid." By A. G. PERKIN.

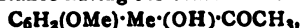
The principal product of the action of methylic iodide upon β -resorcylic acid is a substance crystallising in needles melting at $76-77^\circ$, and having the constitution $C_6H_3 \cdot Me(OMe) \cdot OH \cdot COOMe$. It appears probable that

the hydroxyl group in β -resorcylic acid, which resists methylation, is in the *o*-position to the carboxyl group.

The principal product of the action of ethylic iodide upon β -resorcylic acid is insoluble in alkalis, and contains but two ethoxy groups. It has the formula—

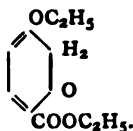
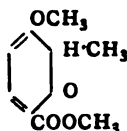


The action of methylic iodide upon resacetophenone has been studied, but the results have been anticipated by Gregor (*Monatsh.*, 1894, xv., 437). The principal product is a substance having the constitution—



insoluble in alkalis, and resembling the results of the action of methylic iodide upon β -resorcylic acid.

It appears probable that the insolubility of the methyl and ethyl ethers of β -resorcylic acid and resacetophenone, which apparently contain a free hydroxyl group, is due to the fact that the oxygen of this latter has assumed the ketonic form. The constitution of the two former substances would therefore be—



Preliminary experiments on the methylation of gallacetophenone have yielded a substance melting at $76-77^\circ$, apparently a dimethyl ether, $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{OH}\cdot\text{CO}\cdot\text{CH}_3$.

Gallacetophenone oxime, $\text{C}_6\text{H}_3(\text{OH})_3\cdot\text{C}\cdot\text{NOH}\cdot\text{CH}_3$, and quinacetophenone oxime, $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{C}\cdot\text{NOH}\cdot\text{CH}_3$, were also obtained.

114. "Note on the Gravimetric Estimation of Maltose by Fehling's Solution." By T. A. GLENDINNING.

The specific cupric-reducing power of maltose possesses a different value according to whether potash or soda is the alkali employed in the preparation of Fehling's solution. Under the conditions of experiment given, the reducing powers to be attributed to maltose are—

Soda, $\text{K}_3.86=61$. Potash, $\text{K}_3.86=64$.

On making comparative analyses of starch-transformation products with the two kinds of Fehling's solution, identical results were obtained, provided the respective values of K were used.

No such difference occurs in the case of dextrose or of invert sugar.

115. "Studies in the Malonic Acid Series." By S. RUHEMANN, Ph.D., M.A., and K. J. P. ORTON, B.A.

The authors have investigated the action of ammonia, hydrazine, and phenylhydrazine on dibromomalonamide. Ammonia yields diaminomalonamide, $\text{C}(\text{NH}_2)_2(\text{CONH}_2)_2$; and hydrazine and phenylhydrazine give the hydrazone and phenylhydrazone respectively of malonamide.

Fuming nitric acid acts on malonamide, forming nitromalonamide. Aniline, when heated with nitromalonamide until ammonia ceases to come off, yields diphenylurea.

On reduction of nitromalonamide with sodium amalgam, aminomalononic acid is obtained.

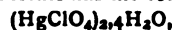
By permission of Professor Claisen, the authors have investigated the action of hydrazine hydrate on ethyl ethoxymethylenemalonate. They obtain a result which does not agree with that of V. Rothenberg.

116. "Mercury Perchlorates." By M. CHIKASHIGE.

Mercuric perchlorate is not anhydrous, its composition being $\text{Hg}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$. It slowly loses, in a desiccator, acid and water, and effloresces. In the air it is very deliquescent (Serullas). When heated, it melts completely at 34° (in dry air); as the temperature rises to 150° , it very slowly decomposes, giving off water and perchloric acid, while a white basic perchlorate, $\text{Hg}_3\text{O}_2(\text{ClO}_4)_2$, is permanent at that temperature. If the salt is heated a long narrow tube, it may be kept in a bath at 400° .

for any time, without permanent decomposition, boiling freely and retaining its transparency, and, when cooled, solidifying unchanged. Whilst heated it is, however, continuously decomposing into basic salt and acid water; but as the acid and water vapours condense and flow back, the salt is continuously re-formed, and presents only the phenomena of ebullition.

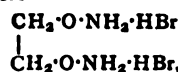
Mercurous perchlorate has the composition—



according to the author; Roscoe found $6\text{H}_2\text{O}$. In a vacuum desiccator it loses in two weeks $2\text{H}_2\text{O}$ and a very little acid, and then ceases to lose weight. It is slowly decomposed by heat, even at 100° or less, in dry air, first losing water and perchloric acid; then gradually, from 150° upwards, becoming mercuric salt, and yielding chlorides and a little chlorate. It resembles mercuric perchlorate in its decomposition, but does not show the phenomena of fusion and ebullition. According to Roscoe, mercurous perchlorate does not lose weight in a vacuum over sulphuric acid, or at 100° .

117. "a-Ethylene Dihydroxylamine Dihydrobromide." By C. M. LUXMOORE, D.Sc.

When ethylene bromide is heated with a solution of hydroxylamine in methyl alcohol to 100° , two mols. of the latter combine with one of the former to form the dihydrobromide of ethylene dihydroxylamine, a white crystalline substance, soluble in water and alcohol, insoluble in ether. When reduced with hydriodic acid, all the nitrogen is obtained as ammonia. The constitution of the substance is therefore—



and its formation lends some support to the view that free hydroxylamine has the structure $\text{O}=\text{NH}_2$.

Ethylene oxide also reacts with hydroxylamine, forming apparently the base corresponding with the hydrobromide described above.

118. "The alleged Isomerism of Potassium Nitrososulphate." By C. M. LUXMOORE, D.Sc.

Potassium nitrososulphate, whether prepared by the absorption of nitric oxide, by potassium sulphite, or by the absorption of a mixture of sulphur dioxide and nitric oxide by potassium hydroxide, has always the same properties. Hantzsch's silver salt, $(\text{KAgSN}_2\text{O}_5)$, has been obtained from specimens prepared in these different ways, and showed the characteristic behaviour described by him.

Potassium nitrososulphate reaches a temperature of about 134° (as indicated by a thermometer embedded in the salt) before it explodes, the gradual and quiescent decomposition into potassium sulphate and nitrous oxide that precedes the explosion furnishing the heat that raises the temperature of the substance above that of the bath in which it is heated.

Pelouze's account of the properties of this substance can be completely reconciled with the recent observations of Hantzsch and of Divers and Haga, with the exception of the statement that it loses no weight when heated to 110° , which is evidently a mistake. Five minutes' heating below 105° causes a loss of weight of 2½ per cent.

There is no evidence to warrant the suggestion of Hantzsch that Raschig's first salt is isomeric with potassium nitrososulphate, nor can it be regarded as identical with the salt prepared by Davy and Pelouze.

119. "On the Freezing-points of Silver and Gold." By C. T. HEYCOCK, F.R.S., and F. H. NEVILLE.

The authors draw attention to the close agreement between the determination of the freezing-point of gold, by Callendar, in 1892, and their own determinations in 1894. The platinum temperatures differ by a few degrees, but, when reduced to the scale of the air thermometer by the same method, the two results do not differ by more than

one degree. The authors further consider the influence of various gases on the freezing-point of silver. They find that the highest and steadiest freezing-points are obtained in the presence of free hydrogen or of coal-gas, and that nitrogen or carbon dioxide produce little or no depression. They find that the well-known effect of oxygen on the freezing-point of silver may amount in extreme cases to a depression of $20^{\circ}\text{C}.$, but that the oxygen can be removed by the action of nitrogen or hydrogen.

NOTICES OF BOOKS.

The Origin and Rationale of Colliery Explosions:

Founded upon an Examination of the Explosions at the Timsbury, Albion, Malago Vale, and Llanerch Collieries; and upon the principal phenomena of the Disasters at the Abercarne, Alltofts, Altham, Apedale, Blantyre, Bryn, Clifton Hall, Dinas, Elemore, Hyde, Llan, Mardy, Morfa, Mossfields, National, Penygraig, Risca, Seaham, Trimdon Grange, Tudhoe, Udstone, and West Stanley Collieries. By DONALD M. D. STUART, F.G.S., Mining and Civil Engineer, Author of "Coal-Dust an Explosive Agent." Bristol: J. Wright and Co. London: Simpkin, Marshall, and Co., Lim. New York: Hirschfeld Bros. 1895. Crown 4to., pp. 144. With two Plans.

WHEN colliery explosions first began to attract public attention, they were considered solely due to so-called "fire-damp," i.e., methane or light hydrogen carbide, which if mingled with atmospheric air forms, of course, a violently explosive total. To combat this serious evil, two distinct methods were devised. On the one hand, the ventilation of the mines was improved so that methane might be swept away as rapidly as it was generated, and might not be anywhere present in the mine in an explosive quantity. On the other hand, there was the safety-lamp in its various modifications which was to prevent any inflammable gas from being ignited by the lights used by the colliers in working. That much disaster was prevented by these two agencies is beyond all question; but still explosions occurred from time to time, though less frequently in proportion to the number of men employed underground and the weight of coal raised. To account for these calamities it was alleged that the ventilation was defective, or that the men carried down matches or picked the lock of their safety-lamps. Both these charges were doubtless true in not a few cases; but there still remained a balance of mischief not yet accounted for. It was therefore suspected—and it was ultimately demonstrated—that there must exist some other agent which might give rise to explosions, either alone or in conjunction with methane. This was found to be coal-dust, which has been studied by Prof. Galloway, and to a greater extent by the present author. Still, however, it was contended by some experts that coal-dust alone, in the total absence of methane, could not occasion an explosion. The Timsbury disaster, however, supplied the needed crucial instance. The Timsbury collieries have been worked with open lights for about seventy years, and during all the working no fire-damp has been detected. The character of the explosion, which took place in the present year, differed entirely in its features from those unquestionably due to fire-damp. In the latter, a blast seems to have swept through the workings, from end to end, occasioning wreckage everywhere. In the Timsbury disaster we have a series of eighteen distinct explosions at very considerable distances from each other. At the points of these explosions there was the usual devastation, falls of roof, shattered doors, &c., but in the intermediate spaces there was no evidence of violent forces.

A further characteristic of the two kinds of explosions appears on comparing the after-damp. Where carbonic

acid is present in quantities exceeding 2.21 per cent, candles are instantly extinguished. The first physiological action encountered is difficulty of breathing, which becomes very marked if the proportion of carbon dioxide reaches 3.38 per cent. Persons who have been exposed to such an atmosphere compare its effects to those produced by violent running; whilst, according to Dr. Haldane, a proportion of 8 per cent is fatal.

The effects of "white-damp" are different; lights are not extinguished, so that the only indication of danger is the physiological action. There is felt a smarting in the eyes and nose, the legs tremble, and giddiness is experienced, and there is imminent danger unless an instant retreat into the air is practicable. In the spaces intermediate between the points of explosion some of the men were found lying dead, but not mutilated, and their lamps had not been extinguished, but in some cases had gone on burning until all their oil was consumed.

At an explosion in a similar non-fery mine (Malago Vale colliery) "the night bailiff was found unconscious, his safety-lamp in his hand, still burning, though it had been exposed to the entire gaseous products of the explosion for nearly two hours."

The immediate cause of the explosion at the Timsbury colliery seems to have been the remarkably dry condition of the mine and the error of James Carter, who seems, in firing a "shot," to have used a much larger quantity of powder than was necessary, and to have used as tamping a mixture of coal-dust and oil. The excessive charge was partly blown out into the dry coal-dust, and set up a process of destructive distillation, liberating combustible gases. It will be perceived on inspecting the plan that the successive explosions took place where the gases met with a sufficient volume of air (i.e., oxygen) to form an explosive mixture.

Mr. Stuart's recommendation for the prevention of similar catastrophes is highly judicious. He proposes that in such dry mines the coal-dust should be kept well and permanently moist; especially at the spots where a shot is to be fired the floor and the sides should be rendered quite sloppy. The evaporation of such a quantity of moisture would consume any unnecessary and dangerous heat-energy.

Concerning the proposed use of "high" explosives in place of powder for blasting, the author does not consider that our experimental knowledge is sufficient to admit of a decision.

Mr. Stuart, by the production of this unpretending work, has laid the mining interests of this country under deep obligation.

Our Chemistry of Nutrition: a Contribution to the Doctrine of Foods and Nutriment. ("Unsere Nahrungs-Chemie: ein Beitrag zur Futter und Nahrungsmittel lehre"). By EMIL PORT. Munich: Theodor Ackermann. 1895. 8vo., pp. 104.

THE author, whilst duly recognising the value of the initial steps taken by Boussingault and Liebig towards a chemico-physiological development of the principles of animal nutrition, complains, with the fullest right, that we have come to a lamentable stand-still. The attempt to decide summarily on the nutritive value of the different foods according to their percentage of certain constituent groups is, he reminds us, as one-sided as that to determine the fertility of a soil simply by the proportions of nitrogen, potassium, and phosphoric acid. He submits the following propositions:—In order to determine the value of a food, it is necessary to ascertain in what forms it contains those substances which directly or indirectly take part in the nutrition of the animal body. Nor must we forget that we have not yet even an approximate knowledge of the individual constituents of foods.

The nutritive effect of a food varies according as it is to be supplied to ruminants, to horses, or to swine. Nor must the physical structure of a food be neglected.

Different races, and even individuals of one and the same race, have a different power of utilising food.

The value of the constituents of food is very unequal, according as the animals consuming them are destined to yield milk, flesh, fat, to exert mechanical power, or are reserved for propagation.

Finally, before we can decide on the nutrient value of any substance, we must learn in what state or admixture it is supplied for consumption.

The author shows that digestion is a far more complicated process than it is commonly supposed. In addition to that form of digestion effected by the secretions of the animal concerned, there is also a "microbic digestion," effected by the micro-organisms which accompany the food, especially of the herbivora. We have never met with an account of the results of a course of experiments made—or proposed to be made?—by Pasteur to decide on effects of diet completely sterilised.

In connection with these propositions, the author puts forward a number of interesting questions concerning the known action of minimal quantities of certain foods or condiments. Here there is urgent need for careful experimentation. This brings Herr Pott to the question of the flavours and odours of foods, and to the consumption of articles which can scarcely be comprised under the two categories of frame-foods or heat-foods. The recent outcry against so-called excitants or stimulants (coffee, beer, wine, &c., in the case of man) applies also to the lower animals, and with equal injustice. Von Pettenkofer, in reply to the agitators who proscribe all "stimulants," irrespective of proportion, points out that these substances act like lubricants in machinery, which do not enable us, *e.g.*, to dispense with steam-power, but increase its efficiency and save the machinery from needless wear and tear. The common sense of mankind has shown us—as the author quotes from C. von Voit—that what we eat with repugnance, or even with indifference, is of little value to the system.

This little book is so full of passages which suggest, not merely reflection, but experiment, that we must here conclude our scrutiny. We can merely glance at a passage in which it is pointed out that "irrigation hay" is deficient, not merely in odoriferous appetising principles, but also in albumen and phosphoric acid.

CORRESPONDENCE.

ON THE

INADEQUACY OF AIDS AND FACILITIES FOR SCIENTIFIC RESEARCH.

To the Editor of the Chemical News.

SIR,—I have just read in the CHEMICAL NEWS (vol. lxxii., p. 224) that, in eulogising very deservedly the work of Professor Runge, it was remarked by Dr. Johnstone Stoney that "it would be very advisable at this juncture to call attention to the unfortunate position in which scientific investigation in the British Islands stood in comparison with that of at least one other country in Europe. There was no scientific man in these islands who possessed a laboratory furnished with the appliances for carrying on such investigations as those which had just been placed before the meeting." "An apparatus which would measure the half or the third of a tenth-metre would really do nothing in an investigation of this kind; they must procure apparatus like the splendid apparatus in Hanover, which would measure to the fiftieth part of a tenth-metre with certainty."

Dr. Armstrong (intervening) said he should like, on behalf of the chemists, who had not said anything up to that time, to express the universal admiration which they

must all have of the communications just made to the meeting. He had risen at this juncture not merely with the object of saying this, but also in order to correct the impression which Dr. Johnstone Stoney had just endeavoured to make at the instigation of Professor Lodge, that they were not capable of doing this kind of work in the British Isles." The Doctor went on to say that this work had been done by individual effort after the fashion usual in England. "If the idea of making such investigations as these occurred to men in this country, who had the requisite capacity for undertaking them, he was sure the effort would always be made."

I can quite appreciate the justice of the remarks of Dr. Johnstone Stoney, than whom no one could be better qualified to speak on this subject, of the small encouragement and the inadequacy of the aids given to such scientific investigations in Great Britain and Ireland.

According to my experience Dr. Armstrong was not happy in his remarks.

It must be now some eight or ten years since Dr. Johnstone Stoney and I had a conversation on the desirability of having a 20-foot Rowland concave grating mounted in Dublin, and fitted with all appliances for the investigation of spectra. Such an apparatus being necessary for the determination of certain physical constants, ought certainly to be provided. There were no funds and no building available. This has a bearing on the following circumstances:—In March, 1882, there was published in the *Journal of the Chemical Society* a paper of mine, entitled "Note on Certain Photographs of the Ultra-violet Spectra of Elementary Bodies," in which it was shown that by photographing the spectra of certain well-defined groups of elements in series, the grouping and the characters of the principal lines are referable to the Periodic Law.

This paper was merely the preface to two others; the first, "On Homologous Spectra," published in September, 1883, in the *Journ. Chem. Soc.*; the second, "On the Spectrum of Beryllium, with Observations relative to the Position of that Metal among the Elements," published in June, 1883. Owing to some untoward circumstance the former paper, which was read first, was long delayed in publication, and finally an uncorrected proof was printed. On drawing attention to this, the remark was casually made to me that it did not matter, as no one would ever read the paper.

It is now necessary to mention that this paper contains the following passage with reference to homologous spectra—that is to say, those spectra which are similarly constituted:—

"The foregoing data present a considerable addition to the body of evidence in support of the view that elements whose atomic weights differ by a constant quantity, and whose chemical character is similar, are truly homologous, or, in other words, are the same kind of matter in different states of condensation. Their particles are vibrating in the same manner, but with different velocities." (See "British Association Report, 1883").

J. R. Rydberg, in 1890, contributed to the *Transactions of the Royal Academy of Sweden* a paper entitled "Recherches sur la Constitution des Spectres d'Emission des Éléments Chimiques," in which he states that among the special contributions to the knowledge of the constitution of spectra, "the observation of M. Hartley upon the constant differences of the number of the oscillations of the components of the double rays of an element is of very great importance."

M. Rydberg had remarked upon the double rays of a number of elements in 1885, but recognised the fact that I had already called attention to this subject; and he then enunciates the law as follows:—

"The difference between the oscillation-frequencies (or numbers proportional to them) of the component of a double ray is constant for all the double rays of the same species in the same element." He adds the words, "this relation applies also to the components corresponding to

triplets." My paper dealt with triplets and other groups, as well as with double lines; it further treated of rays with certain characters in common; hence it became necessary, in order to include the cases of triplets, to modify the statement of the law.

Mr. J. S. Ames, in the *Phil. Mag.*, vol. xxx., p. 33, 1890, recognised the law of homology in the spectra of the elements as pointed out in my paper, and to him, as well as to M. Rydberg, my thanks are due. M. Rydberg, however, remarks that, as Mr. Hartley has not made further use of the excellent materials which he has obtained by his measurements in the ultra-violet spectra, it may be concluded that he has not attributed much importance to the relations found. The previous quotation, which for the purpose of easy reference is in this letter printed in italics, will, I think, show that I was fully alive to the importance of the facts observed, and, indeed, at a later date it led to the enunciation of the following modification of the Periodic Law:—*The properties of the atoms are a periodic function of their masses;*" and, further, it led to the view which I have taken care to inculcate at various lectures during the past ten years, that, in well-defined groups, the properties of the atoms are absolutely a function of their masses.

In other words, *one element in a group differs in its properties from another, not because it consists of another kind of matter, but because the quantity of matter in an atom of it is different.*

No one can study homologous spectra without being convinced of the enormous importance to the chemist of a thorough investigation into their constitution. To this end it was my particular desire to obtain the use of a large dynamo and gas-engine for producing arc spectra on an adequate scale, and by Rowland's method to photograph them for the purpose of carefully studying the numerical relations between the oscillation-frequencies of similarly constituted groups of lines both in arc and spark spectra. For some time there seemed to be a prospect of the Science and Art Department supplying the electric current suitable for such researches; but it was found that, even had this been done, there was no place within the Royal College of Science where the grating could be mounted and used.

An application was made to the Committee of Section B of the British Association, when it met at Southampton, for a sum of money in aid of the investigation of arc spectra of the elements; but this was not granted. I had already spent a considerable sum in such researches, and had used, for instance, a 6 foot concave grating, but it was found to be of little value.

After fruitless endeavours to obtain the means to carry on the work in a proper manner, the projected investigation went into abeyance. In the meantime Messrs. Kayser and Runge commenced their work "*Ueber die Spectren der Elemente.*" In the *Vierte Abschnitt*, 1891, they refer to my previous investigation, and of course have greatly extended it.

The recital of the foregoing facts will, I think, be found contradictory to the statement of Dr. Armstrong, which, as he admits, was intended to reverse the effect of Dr. Stoney's remarks, and which happened to be singularly inappropriate.

The assistance which I had sought in more than one quarter was not forthcoming, and it certainly appears as if this was due to a want of appreciation among chemists in England of the importance to be attached to an accurate study of spectra.

I may add that it has been a source of the greatest pleasure and satisfaction to me, for the last four years, to observe that the results published by Professors Kayser and Runge have realised what I had been led to expect from observations made years ago with the imperfect means at my command.—I am, &c.,

W. N. HARTLEY.

Royal College of Science, Dublin.
November 9, 1895.

CANE-SUGAR AND CITRIC ACID.

To the Editor of the Chemical News.

SIR,—If your readers will kindly compare my three notes on this subject with that published by Messrs. Searle and Tankard (*CHEMICAL NEWS*, vol. lxxii., p. 235), they will see that these gentlemen, who profess to have repeated my experiments, have not done so at all, or at least only partially and unsuccessfully.

I hope to publish later a more complete account, but I have not been able to work for more than six weeks past. I may state, however, that according to the respective quantities of permanganic acid and sugar, according as sulphuric or nitric acid is used, and according to the temperature of the day, the products vary considerably.

In my experiments tartaric acid, citric acid, saccharic acid, and formic acid have been certainly produced, and the two first have been separated and crystallised from alcohol. It is perhaps needless to add that citrate of lime is not precipitated by boiling unless the liquid is of a proper degree of concentration and neutral.

It would be interesting if Messrs. Searle and Tankard would tell us what becomes of the sugar in their experiments. If they do not get the acids I have mentioned, what do they get?—I am, &c.,

T. L. PHIPSON, Ph.D.

The Casa Mia Laboratory, Putney,
November 16, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Zeitschrift für Analytische Chemie.

Vol. xxxiv., Part 2, 1895.

Reagent for Monovalent Alcohols.—Bela von Bitto (*Chemiker Zeitung*).—The author mentions that Schön's reaction takes place only with absolute alcohol, whilst the reactions of Lieben and Landwehr indicate other substances. Hence he proposes a solution of 0.5 methyl violet in 1000 c.c. water. He adds 1 to 2 c.c. of this solution to the liquid in question, adds $\frac{1}{2}$ to 1 c.c. of the solution of an alkaline polysulphide, and shakes up. In presence of monovalent alcohols the liquid turns cherry-red to violet-red, and remains clear. If no monovalent alcohols are present the solution takes a greenish blue colour, and after some time deposits reddish violet flocks, whilst the supernatant liquid becomes yellow. Bi- and polyvalent alcohols, carbohydrates, acids, aromatic compounds, phenols, &c., do not yield this reaction. With methylic and ethylic alcohols, normal and isopropylic alcohol, the colour is a cherry-red; with tertiary butylic alcohol, isobutylic alcohol, isobutylcarbinol, and allyl alcohol the colour is a violet-red.

Comparative Studies on the three Isomeric Nitrobenzoic Acids.—Oechsner de Coninck.—From the *Comptes Rendus*.

Distinction between Aldehyds and Ketones, especially Aldehydic and Ketonic Sugars.—From the *Comptes Rendus*.

Differences in the Behaviour of Tannin Substances with Reagents.—R. Procter (*Der Gerber*).—The author divides the tannins into the following four classes:—Those related to pyrocatechin; those of mixed or unknown origin; those derived from pyrogallol; and those containing ellago-tannic acid. As reagents he uses the following solutions:—(a) Iron-alum, a 1 per cent solution, instead of ferric chloride; the colour produced is observed *at once*. (b) Bromine water added to the tannin solution until it smells distinctly of bromine, observing whether a precipitate is pro-

duced or not. (c) Copper sulphate, a 1 per cent solution in slight excess, observing whether the precipitate is soluble in ammonia or not. (d) Nitrous acid; to a few c.c. of the dilute tanning solution there are added a few crystals of potassium nitrite and then 3 to 5 drops of decinormal sulphuric or hydrochloric acid. The solution is either at once red, and passes through violet slowly into deep indigo-blue, or there appears only a yellow or brown colouration or a precipitate (see tables). (e) Stannous chloride and hydrochloric acid; 10 c.c. of the concentrated solution is added to 1 c.c. of the solution of the tannin; the colour is observed after standing for ten minutes. (f) Pine shavings and hydrochloric acid. *Reaction for Phloroglucol*.—A shaving of pine wood is moistened with the tanning solution, and, when dry, is moistened again with concentrated hydrochloric acid; in presence of phloroglucol, there appears at once a light red colour; catechin and gambier give the reaction distinctly. (g) Sodium sulphite; to a few drops of the solution of tanning matter there is added a crystal of this salt; with valonia, there appears at once a purple-red colour. (h) Concentrated sulphuric acid; a small test-tube is rinsed out with the solution of tannin, which is then poured out so that only a small drop remains, and the sulphuric acid is cautiously substratified. The coloured ring at the plane of contact is observed, the liquids mixed and diluted with water. (i) Lime water; the reactions are preferably obtained in a porcelain capsule; an excess of the reagent is not injurious, but it must then be allowed to stand for some time. The strength of the tannin solution must be so adjusted that 0.6 grm. solid residue are contained in 100 c.c. The author's observations are given in detail in the form of tables. Upon them follow, also in tabular form, the earlier observations of Andreasch.

Detection of Hydroxylamine.—A. Angeli (*Gazz. Chimica Italiana*).—The author mixes the neutral solution with sodium nitroprusside and renders it strongly alkaline with soda-lye. On applying heat there appears at once a fine magenta colour. An excess of ammonium salts interferes. Hydrazin and other inorganic reducing agents do not give the above reaction. Phenylhydrazin gives in the cold a red colour, which disappears on heating.

Elementary Analysis of Highly Volatile Organic Substances.—G. Perrin.—The author makes use of a special apparatus resembling that used by Zulkowsky and Lepex for halogens and sulphuretted substances.

Quantitative Determination of Hydrazin in its Salts.—Julius Petersen (*Zeit. Anorg. Chemie*).

Determination of β -Naphthol.—Küster (*Berichte*).—The author appends a table of corrections to his former method.

Volumetric Determination of Naphthalin, Acenaphthen, α - and β -Naphthol, and Analogous Substances.—F. W. Küster (*Berichte*).—The author's method depends on the circumstance that these substances form insoluble compounds with picric acid.

Determination of Antipyrin.—F. Schaak (*American Journal of Pharmacy*).—The author has devised a colorimetric process depending on the formation of nitroso-antipyrin; its bluish green colour can be recognised in dilutions of 1 : 20000.

Gravimetric Determination of Sugar with Fehling's Liquor.—G. Gaud.—From the *Comptes Rendus*.

Determination of the Atomic Weight of Bismuth.—R. Schneider.—From the *Journ. Prakt. Chemie*.

Atomic Weights of Nickel and Cobalt.—R. Schneider.—The mean value obtained for nickel is 58.7433, and that for cobalt 59.3507.

MEETINGS FOR THE WEEK.

WEDNESDAY, 27th.—Society of Arts, 8. "Locomotive Carriages for Common Roads," by H. H. Cunyngname.

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THE CHEMICAL NEWS.

VOL. LXXII., No. 1879.

ON THE ATOMIC WEIGHT OF HELIUM.

By N. A. LANGLET.

ALTHOUGH the unitary character of helium may still appear questionable, it will be not uninteresting to obtain an approximate determination of its atomic weight, or at least of the mean atomic weight of its constituents, in order thus to obtain some light on the position of this peculiar substance with relation to known elements. After succeeding in obtaining pure helium, *i.e.*, a gas which displays in Geissler's tube only the spectral lines ascribed to the hypothetical solar element "helium," I have undertaken a determination of its density as accurately as the small quantities of the gas at my disposal permitted.

The helium used in the determinations was prepared and purified as follows:—A tube of a metre in length, of sparingly fusible glass, was charged with a layer of manganese carbonate of 10 c.m. in length, and then filled up almost to one-half with a mixture of (3 parts) pulverised cleveite and (2 parts) potassium pyrosulphate. At about 20 c.m. from the mouth a plug of asbestos was introduced, and the tube was then filled with a stratum of 10 c.m. of coarsely granular copper oxide. After the mixture was spread out in the tube, the copper oxide was heated to redness, and the air, as far as possible, expelled by carbonic acid. The mixture was then heated for a few moments in its entire length, and the gas evolved at first was expelled by carbonic acid to remove any air which might be present. The mixture was then, as in organic analysis, slowly heated to full redness (commencing at the front), and the gas which is briskly evolved was collected in an apparatus resembling Schiff's nitrometer over potassa-lye at 50 per cent. In order to be freed from the last traces of nitrogen, hydrogen, and water, the gas was passed through a long tube of 1 c.m. in thickness (of sparingly fusible glass) which contained, in succession, layers of copper oxide, phosphorus pentoxide, and powdered magnesium. The copper oxide and the magnesium were heated to strong redness. From this tube the gas passed directly into a glass globe holding 100 c.c., and previously carefully exhausted. In this manner the density was found to be 0.139 (air=1), or 2.00 (H=1). After weighing, the globe was evacuated, the gas pumped back into the gasometer, and again led through the ignited tube into the globe. The weight of the gas had not varied, and the density was again determined as 0.139. A small quantity of the gas was passed from the globe into a Geissler tube, and its purity was tested spectroscopically. It was found perfectly free from nitrogen, hydrogen, and argon. A determination (made by opportunity of an examination of the specific heat of helium) of a quantity of the gas obtained and purified by the same method gave the value 0.140. Though these determinations cannot claim any great accuracy, on account of the small quantities of the gases employed, we may, without much error, fix the specific gravity at 0.14 (air=1), or 2.0 (H=1).

The atomic weight will then be either 2 or 4, according as the mol. contains 2 or 1 atoms. To decide this question, the speed of sound in helium was determined, and from this the proportion was calculated between the specific heat at a constant pressure and at a constant volume. For this purpose the gas was placed in a tube closed at one end by means of a perforated caoutchouc stopper. Over the other end a membrane of caoutchouc was extended air-tight, upon which a plate of glass was cemented with tallow. The tube was then evacuated by means of a narrow tube inserted in the caoutchouc stopper

and filled with helium. After the glass plate had been removed, a powerful stream of air was directed rather obliquely through a narrower tube against the membrane, and thus sounds were obtained, the wave-lengths of which could be measured by means of some silicon dioxide introduced into the tube and set in motion by the vibrations. From the speed of the sound found in this manner the relation between the two heat capacities was calculated as 1.67. The low density of helium renders the determinations uncommonly difficult and somewhat uncertain.

The molecule of helium contains, therefore, like that of argon, only 1 atom. The atomic weight must therefore be taken as = 4.

Ramsay, after having in a preliminary communication indicated the specific gravity of helium as 3.88 (H=1), has lately published an extended examination of the helium obtained from different minerals. The numbers which he obtains do not differ greatly from each other, the mean of all the determinations being 2.18, *i.e.*, 8 or 9 per cent higher than the value which I have found. If helium, as Lockyer and Deslandres have assumed, is not a simple gas, but a mixture of several, the difference would be easily explained. But as Ramsay appears to have made no spectroscopic examination of the purity of the helium which he experimented upon, it is naturally not impossible that, in spite of careful purification, it may have retained slight impurities of nitrogen or argon. If the density which I have obtained can be regarded as correct, Ramsay's helium would contain a mean of 1.5 per cent by volume of nitrogen, or 1 vol. per cent of argon.

When this research was undertaken, Ramsay had obtained from his cleveite merely a mixture of helium with argon, and it seemed not possible to separate both gases from each other. But as I obtained pure helium (as far as it can be ascertained with the spectroscope) from the mineral at my disposal, and it was scarcely possible to assume that the argon studied by Ramsay could be found to be derived from the atmosphere, its absence can be attributed only to an accident which may possibly never recur.

I submit that by these circumstances the apparent intrusion into a region which belongs to the discoverer of helium will be explained and permitted.—*Zeitschrift für Anorganische Chemie*, x., p. 287.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 250).

CHAPTER II.

ON THE NATURE AND AMOUNT OF SOLUBLE AND INSOLUBLE MINERAL MATTERS, IN THE AIR AT THE HIGHER DISTRICT OF BRUSSELS, AND IN RAIN WATER, AT GIVEN TIMES AND UNDER GIVEN CONDITIONS.

ONE knows, from researches made in different places at given times, that air may contain soluble and insoluble compounds of sodium, calcium, and potassium, together with many insoluble silicates. The late Robert Angus Smith reviewed our knowledge of this subject in his standard work "Air and Rain."

Judging by the very great trouble experienced during spectroscopic observations of flames burning in the air of Brussels and the neighbourhood, one is tempted to believe in the existence of large quantities of sodium compounds, such as sulphates and chlorides, in the air of this town. Researches that I have undertaken at very different periods have convinced me that this opinion is erroneous,

* "Air and Rain," by Robert Angus Smith. London: Longmans and Co. 1872.

at least as regards the higher part of the town, where my experiments were made. As a matter of fact, when taking from *ten to fifteen cubic metres* of air as a unit of volume, one cannot measure the amount of soluble sodium compounds present. It is not so with insoluble compounds of sodium and calcium.

In order to ascertain the quantity of solids suspended in free air, when it was *as still as possible*, I condensed the water vapour which exists in such variable quantities. It seemed to me, in fact, that, *during the process of condensation, the water ought to entrap all particles, of whatever material, suspended in the layer of air in contact with a surface chilled below dew-point.* I effected this condensation on the outer surface of a polished platinum apparatus which had been recently washed and then heated to redness. The apparatus I used consisted of a cylindrical platinum refrigerator with a domed top, 20 c.m. diameter by 30 c.m. height.

The domed top, fitting loosely on the vessel, reached 2 c.m. down it, and was provided with a long collar and a large tube in the centre. The vessel was two-thirds filled with disulphide of carbon; in the opening in the lid was fitted a cork, pierced by a glass tube for bringing a current of dry air to the disulphide of carbon, and by a thermometer registering $\frac{1}{10}$ th of a degree C.. The air current was made by bellows or a water-pump, and was dried before reaching the disulphide of carbon. When the water-pressure was constant, the bellows were able to regulate the current so as to obtain and keep a sufficiently low temperature to bring the walls of the vessel below dew-point, and as near as possible to 0° C., without freezing the condensation water.*

To the collar of the domed top was fitted a cork pierced by a glass tube, meant to conduct away the air saturated with disulphide of carbon vapour.

During use the apparatus was freely suspended in a slightly inclined position, in order to assist the fall of the water. A platinum sheet served to lead the water, as it was condensed, into a platinum funnel containing a double filter-paper washed in succession with dilute nitric acid, with pure water, with dilute hydrofluoric acid, and again with pure water, touched at one point the lower part of the bottom of the vessel.

The spout of the platinum funnel passed through a hole in a glass plate which supported the funnel, and was itself supported by a small platinum dish recently washed and ignited to redness, meant to receive the filtered water of condensation.

I then ascertained the amount of water collected, by weighing it in a covered platinum crucible.

To determine the nature and weight of the bodies left in the filter, I made the following arrangements:—

Into a platinum dish, of 110 cubic c.m. capacity, previously washed and ignited to redness and furnished with a spout, was measured *one hundred grms.* of filtered water, which was then evaporated on a bath. When the water was evaporated down to about 1 c.c., the liquid was transferred into a very small well-polished platinum dish, weighing about *one grm.*, and the weight of which I had determined to within *two or three thousandths of a m.grm.* After evaporating the liquid from the very small platinum dish on the bath, I put into it the washings from the larger dish, and evaporated the whole to a constant weight. I then weighed and determined the nature of the residue. I tested for chlorides with nitrate of silver, and for sulphates with chloride of barium.

The filters, through which the condensation water had been passed, were then dried. The inner filter was com-

pared with the outer, and both were examined under a microscope. After this examination the inner filter was folded and re-folded and tied in a fine platinum wire, and carbonised at a low temperature in a closed platinum vessel.

The carbon was carefully put into the outer envelope of a gas jet, to burn it. During combustion one could ascertain, by spectrum analysis, the nature of the spectrum produced.

After combustion I weighed the ash, and determined its constituents by using successively *chloride of ammonium, fluoride of ammonium, and sulphuric acid*, all pure.

The results arrived at were as follows:—

A. Outer Air.—The condensing apparatus was freely suspended outside a window with a south-west exposure, looking on to a garden, 9 metres above the ground, which is 49 metres above the lower part of the tower and 77 metres above sea-level, at about 45 c.m. from the wall,—and a board was used to support articles to be placed outside the window. The apparatus was sheltered from wind from the front and sides, from sun, and rain, by movable screens, also 45 c.m. away from it. Nevertheless the surrounding air could freely penetrate from above and below, as well as circulate in and escape from this enclosed space.

A Bunsen lamp, which could be lighted from inside by opening one of the movable window-panes, was put on the board. This lamp was surmounted by a very large sheet-iron funnel, communicating with a sheet-iron pipe fixed to the wall, to carry off the products of combustion of the coal-gas feeding the lamp. By opening the movable pane in front of the lamp, and bringing forward the spectroscope, one could at any time make a spectrum analysis of the flame, which assisted, as I satisfied myself, to a great extent in the supply of air to the enclosed space.

A thermometer *in the shade*, and identical with that in the top of the apparatus and reaching into the disulphide of carbon, showed the outside temperature.

Having made all arrangements for my experiment, I started the pump *slowly*, so as to bring dry air through the disulphide of carbon and lower the temperature to dew-point. Owing to the considerable size of the apparatus and the care I took, I was able, at every attempt, to fix this point to within about 0.2°.

1st. With a light west wind:—

Temperature of the air	18.5°
Dew point	12.6°
Weight of water condensed ..	125 grms.

Whilst the pump was working, the temperature of the disulphide of carbon was between 0° and 3°, and an analysis of the flame of the Bunsen lamp showed a decided sodium spectrum.

Five drops ($\frac{1}{2}$ c.c.) of a 10 per cent solution of nitrate of silver had a perceptible effect on 10 c.c. of the filtered water contained in a stoppered glass tube, with its bottom flattened and polished, 15 m.m. diameter, and surrounded for its whole length by paper blackened with lamp-black,—a condition in which the least opalescence is easily noticed.

One drop of a saturated solution of chloride of barium had no effect on *ten c.c.* of the filtered water. After evaporating the mixture down to about half a c.c., the liquid was perceptibly clouded.

The evaporation of 100 c.c. of the filtered water, on a bath *in the outer air*, left a small yellowish transparent stain, perceptibly hygroscopic, the weight of which was less than the limit of error of weight,—that is, two or three thousandths of a m.grm.; when heated, this residue perceptibly blackened; when dissolved in a few drops of pure water, it made a solution of which a part, when put on to a fine platinum wire loop recently ignited to redness was entirely volatilised, colouring a Bunsen jet yellow, and showing on analysis a *brilliant*, though temporary, sodium spectrum without a trace of a calcium spectrum,

* During these experiments, when the pressure of the water working the bellows was increased, the water of condensation, instead of being deposited in a liquid state, was frozen. The ice produced was either quite *transparent* or *opaque*, but tinted either with *black*, like smoky quartz, or with *yellowish gray*. An examination under the microscope of this ice, or of the water got by melting it, plainly showed the shape of the foreign bodies mixed with it. I call the attention of any one engaged in researches on the nature of the particles floating in the air to this point.

even after having moistened the loop with a solution of chloride of ammonium.

The inner filter, through which the condensation water had passed, showed, after desiccation, a greyish tint. With a microscope one could see numerous black specks and bright grey specks, as well as a great number of filaments.

The introduction of the carbon, made by carbonising the inner filter in a closed vessel, into the envelope of a Bunsen jet, coloured a great part of it yellow.

During the combustion of the carbon, spectrum analysis showed a sodium spectrum, and a faint and incomplete calcium spectrum, but no trace of the potassium line. The weight of the deep brown siliceous ash was about 0.00085 gm.

The ash, when dissolved in a saturated solution of chloride of ammonium adhering to a fine platinum wire loop, and introduced, after slow desiccation, into a Bunsen jet, showed a strong sodium spectrum and a faint calcium spectrum, but no trace of the potassium line.

The loop, coated with the ash, was moistened thrice with a saturated solution of volatile fluoride of ammonium, heated each time to a dull red heat, to volatilise the siliceous sand and the silica from the silicates, and then put into the envelope of a Bunsen flame; it immediately coloured it yellow. Spectrum analysis of this envelope showed the sodium line, but no trace of a calcium or potassium spectrum.

The platinum wire loop, when moistened with sulphuric acid and put into the flame, coloured it yellow, but spectrum analysis of the flame did not show the potassium line.

Thus the water of condensation contained a trace of sodium in the form of chloride and sulphate, and sodium and calcium in the form of various silicates, whilst silicate of potassium was not present.

2nd. With a total absence of wind:—

Temperature of the air	8.20°
Dew-point	7.95°
Condensed water	125 grms.

At the time of commencing to condense the vapour, fine rain had alternated for three days with damp fog, and the sheltering screens were quite damp. During the time occupied in condensing, which was considerable, the temperature of the disulphide of carbon varied from 0° to 2.5°, and spectrum analysis of the flame burning in air failed to show the sodium line.

Five drops of the 10 per cent solution of nitrate of silver, after waiting for thirty minutes, produced no cloudiness in 10 c.c. of filtered water. When the volume of the mixture was reduced by evaporation to about half a c.c., a cloudiness appeared on cooling it. This was re-dissolved by ammonia.

The liquid formed by the evaporation of 10 c.c. of filtered water down to about half a c.c., was slightly clouded by one drop of a saturated solution of chloride of barium.

One hundred c.c. of filtered water left, on evaporation, a small brown stain, quite distinct under a microscope, and perceptibly hygroscopic. The weight of it was within the limit of error in the weight of the dish (0.003 m. gm.). The stain perceptibly blackened when heated; the residue was dissolved by two drops of water, and the solution, when put into a Bunsen flame, showed the sodium line only.

When the inner filter through which the water passed was dried, it was decidedly grey; when examined under a microscope, it showed numerous small black specks, and also filaments of various lengths. Combustion of the carbon, made by carbonising the filter in a closed vessel, left a trace of decidedly brown ash. During the whole period of combustion I saw the sodium spectrum to the exclusion of any other.

Thus, although I was not able by spectrum analysis to detect the presence of the sodium line in the Bunsen

flame burning in the air which furnished the water of condensation, I nevertheless ascertained that it contained sodium in the form of chloride and sulphate, since the water of condensation contained a trace of these bodies. 3rd. Favourable atmospheric conditions occurring, I checked these latter observations. After five days' drizzle, without sensible wind, and whilst it continued raining,—

The air temperature being	9.45°
And the dew-point	9.15°

I collected by condensation 135 grms. of water.

The screens sheltering the apparatus were thoroughly soaked by the rain. Throughout the time the apparatus was working, the temperature of the disulphide of carbon was between 0° and 2.8°. Spectrum analysis of the Bunsen flame burning in the outer air did not show a glimpse of the sodium line.

Five drops of a 10 per cent solution of nitrate of silver in 10 c.c. of filtered water showed no appreciable precipitate after waiting twenty minutes. When the mixture was evaporated down to about half a c.c. it perceptibly clouded on cooling; this was re-dissolved by ammonia.

Ten c.c. of filtered water were evaporated down to about half a c.c. The liquid was slightly clouded by one drop of a saturated solution of chloride of barium.

One hundred c.c. of filtered water left, on evaporation, a small sparkling brown stain, absolutely unweighable. When heated, the stain turned black; the residue, when dissolved by two drops of water, and put, in the form of a solution, into a Bunsen flame, coloured it yellow. Spectrum analysis of the flame showed a brightly-coloured, but temporary, sodium line.

The inner filter through which the water passed, when dried and compared with the second filter, also dried, had a distinct grey tint on the side which received the water, and showed under the microscope a number of black specks, and also filaments, some long, others short. After burning the carbon made by carbonising the inner filter, there remained a minute trace of brown ash. During the combustion I saw a very faint and transient sodium spectrum.

Thus, although I was not able at any time to detect the sodium line in a Bunsen flame burning in the air, nevertheless the air contained sodium in the form of chloride and sulphate, but in an absolutely unweighable quantity in 15 cubic metres of air.

(To be continued).

THE QUANTITATIVE DETERMINATION OF PERCHLORATES.*

By D. ALBERT KREIDER.

(Concluded from p. 252).

It is necessary of course to prevent the access of air into the bulb until the acid has been neutralised, to accomplish which, without loss of iodine, potassium carbonate must be used, at least for the end reaction. To remove the contents of the bulb for titration the two delivery-tubes were filled with water, after removing all sodium hydrate from the one through which the oxygen was entered; the shorter end connected to a supported funnel containing a saturated solution of bicarbonate, and the longer one inserted into an Erlenmeyer beaker containing a saturated solution of bicarbonate in amount sufficient—as previously determined—to neutralise all the acid taken. By opening that stopcock the delivery-tube of which reaches below the liquid in the beaker, the bicarbonate is drawn in by the partial vacuum, with liberation of sufficient carbon dioxide to force all the

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. 1., October, 1895.

liquid out. Owing to the consequent effervescence as the liquid gains its exit, the flow must be regulated by the stopcock so as to avoid loss of iodine, which is prevented by inclining the beaker so that the bubbles strike against its side instead of being allowed to splutter out of the opening. To wash out the bulb it is raised almost horizontally, so as to prevent the liquid from running through, and the upper stopcock opened to admit the bicarbonate from the funnel. Both stopcocks are then closed, the bulb disconnected and agitated, after which it may be washed with water and admission of air without any fear of liberating more iodine. An excess of decinormal arsenic is then run into the beaker and titrated back with iodine.

The many little precautions essential to note for the manipulation are in practice accomplished in a few moments. Seven determinations (not counting one which was all but completed, when an accident terminated it), from the weighing of the perchlorate to the titration, were completed in one day: and the results recorded in Table VII. show with what reliability. In making the series of experiments recorded in Table VII. it was found expeditious to have a partial vacuum always accessible instead of waiting each time for the exhaustion. This was obtained by connecting a vacuum flask with a two-holed stopper to an ordinary water-pump, and having the other perforation fitted with a glass stopcock. The bulb was merely attached to the vacuum by a piece of rubber tubing; the stopcock opened and closed immediately, by which means a sufficient exhaustion was secured. To have the vacuum always in readiness, a valve, described in a former article of mine (*Amer. Journ. of Science*, l., p. 132), was placed in the rubber leading to the pump, and when lubricated with glycerin would hold the vacuum perfectly. The nitric oxide employed was supplied by a Kipp generator, in which globules of copper were acted upon by nitric acid mixed with an equal volume of water. To purify the gas evolved from any possible trace of the higher oxides, it was first passed through an acidified solution of potassium iodide in Geissler absorption bulbs, the latter one of the three being alkaline. This method of generating nitric oxide in a Kipp generator (preferably charged with dilute acid and kept warm by immersion in hot water when large amounts of the gas are to be drawn at frequent intervals) was devised by Professor Gooch, by whom it has been employed for some time. It is automatic and eminently satisfactory. The hydriodic acid was obtained from a solution of potassium iodide containing 1 grm. in 10 c.c.; 30 c.c. being taken for each experiment, and acidified with the required amount of hydrochloric acid immediately before using, so as to prevent any liberation of iodine by the oxygen of the air. In those experiments in which more than this amount of potassium iodide was employed a correspondingly stronger solution of the latter was used, so that the volume of water was in all cases 30 c.c.

TABLE VII.

	KClO ₄ taken. Grm.	KI taken. Grms.	HCl taken. C.m.s	KClO ₄ found. Grm.	Error. Grm.
(32)	0.1000	3.0	3.0	0.1003	0.0003 +
(33)	0.1000	3.0	3.0	0.1006	0.0006 +
(34)	0.1000	3.0	3.0	0.0998	0.0002 -
(35)	0.1000	4.0	4.0	0.1003	0.0003 +
(36)	0.1000	3.0	3.0	0.1003	0.0003 +
(37)	0.1000	3.0	4.0	0.0999	0.0001 -
(38)	0.1000	3.0	3.0	0.1003	0.0003 +
(39)	0.1000	3.0	4.0	0.1001	0.0001 +
(40)	0.1500	3.0	4.0	0.1493	0.0007 -
(41)	0.2000	6.0	6.0	0.1999	0.0001 -
(42)	0.2000	6.0	6.0	0.2009	0.0009 +
(43)	0.0100	3.0	3.0	0.0099	0.0001 -
(44)	0.0100	3.0	3.0	0.0100	0.0000
(45)	0.0000	3.0	3.0	0.0003	0.0003 +

In experiments (40) and (43), during a momentary pause in the shaking of the bulb during the absorption, a black deposit of iodine began to form on the glass, and the result proves the importance of the precaution previously given, that the hydriodic acid should be kept hurling about the bulb until the action is completed. The blank determination (45) shows a constant error of the process, which is about 0.0003+, and will be seen to correspond very closely to the average error of the determination. The cause is doubtless to be attributed to the trace of air which may remain in the bulb or be dissolved in the water. Since it can easily be determined and the correction made, it does not detract in any degree from the reliability of the determination.

To determine perchloric acid associated with other oxidising agents, it is only necessary to treat the mixture with the reagents which this investigation and the one referred to has shown to accomplish the reduction without affecting the perchlorate; subsequently evaporating to dryness and treating the residue according to the above process, viz., by heating in a current of carbon dioxide until decomposition is complete; collecting the oxygen over caustic potash; allowing it to enter a partial vacuum bulb containing a solution of potassium iodide, hydrochloric acid, and nitric oxide under constant agitation; and determining by means of a standard solution of arsenic the amount of iodine set free. The method is proving applicable also to the determination of oxygen in air, or wherever it may be obtained in the free state, unless diluted to such an extent with other gases that the vacuum would be filled by the diluent; even this contingency could be met by enlargement of the absorption-bulb.

Many helpful suggestions are to be credited to Prof. Gooch.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING OCTOBER 31ST, 1895.

BY WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, *Metropolis Water Act*, 1871.

London, November 11th, 1895.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 189 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Oct. 1st to Oct. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 189 samples examined all were found to be clear, bright, and well filtered.

We have this month to record an excess of rainfall, the quantity measured at Oxford being 2.85 inches, compared with 2.56 inches (the average for 25 years), showing an excess of 0.29 inches. The rain was fairly well distributed throughout the month, though more fell in the first ten days than later on. There were fifteen days on which no rain fell.

Compared with the corresponding month of last year, the quality of the Thames derived waters shows a marked improvement in every respect; and, in spite of a much heavier rainfall than in September last, the results are almost identical.

Our bacteriological examinations give the following results:—

	Colonies per c.c.
Thames water, unfiltered	2603
Thames water, from the clear water wells of the five Thames-derived supplies .. highest	108
Ditto ditto lowest	30
Ditto ditto mean	68
New River water, unfiltered	1577
New River water, from the Company's clear water well	41
River Lea water, unfiltered	3018
River Lea water, from the East London Com- pany's clear water well	48

These results show that the Water Companies are able to successfully cope with the extra strain put upon them, their filtering appliances being in excellent condition.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

ON THE VAPOUR-TENSIONS OF MIXTURES OF VOLATILE LIQUIDS.*

By C. E. LINEBARGER.

(Concluded from p. 251).

The Molecular Mass of Liquid Acetic Acid and a General Method of Determining Molecular Masses of Liquids.

THE data given in the preceding section on the vapour-tensions of mixtures of acetic acid and benzene, taken in connection with the fact that the partial tension of benzene in its solutions is directly proportional to its concentration, permit of determining the molecular mass of the acid when diluted to any degree whatsoever with the hydrocarbon; and this special case may be generalised so as to permit of universal application. Furthermore, if the molecular mass of a substance be known in solutions of every degree of concentration, it is possible by a little extrapolation to pass over to the molecular mass of the pure liquid. It is, of course, assumed in making such an extrapolation that no break occurs in the continuity of the phenomenon, that is, the addition of very small quantities of a normal liquid to an associated one occasions correspondingly small changes in the degree of complexity of the molecules of the latter.

The way in which I have gone about to get at the molecular mass of acetic acid in benzene and toluene solution is as follows:—

In a system of co-ordinates, molecular masses of acetic acid from 0 to 100 were laid off on the axis of abscissæ (20 inches long), and on the axis of ordinates, the vapour-tensions were taken from 0 to 150 m.m. of mercury (15 inches long). A straight line was drawn from the point 100 on the axis of abscissæ and 0 on the right-hand axis of ordinates to the point 0 on the axis of abscissæ and 146 (benzene at 35°, 75.6 (benzene at 20°), and 47.2 (toluene at 35°). Upon this straight line must lie all the points corresponding to the partial tensions of benzene or toluene dissolved in acetic acid. So points were marked along it giving the value of the partial tensions of benzene and toluene in solutions containing 10, 20, 30, &c., per cent of acetic acid, the data being taken from Table XIII.

The value of the abscissæ which these points determine give the number of molecules of acetic acid contained in 100 molecules of the mixture. All that has to be done now is to solve for every case this problem: Given a mixture containing m parts of a liquid A, having a molecular mass x , and n parts of a liquid B, having a molecular mass y ; the mixture is made up of r molecules of A and s molecules of B. What is the value of x in the terms of y , m , n , r , and s ?

In the case before us we will take acetic acid for the liquid A, and benzene, or toluene as the case may be, for B; then n is equal to $(100-m)$ and s to $(100-r)$.

It is easily found that the solution of our problem is—

$$x = \frac{m s y}{r n} \text{ or } x = \frac{m(100-r)y}{(100-m)r}.$$

In the accompanying Tables, XIV., XV., and XVI., the values of m , r , and x are given.

TABLE XIV.

Molecular Mass of Acetic Acid dissolved in Benzene at 35°.

Per cent of $C_2H_4O_2$ in liquid mixture.	Mols. $C_2H_4O_2$ in 100 mols. of liquid mixture.	Molecular mass of acetic acid.
10	5.2	158
20	10.6	164
30	16.6	167
40	23.1	173
50	30.0	182
60	37.7	193
70	47.2	203
80	59.3	213
90	75.6	227
100	100.0	240

TABLE XV.

Molecular Mass of Acetic Acid dissolved in Benzene at 20°.

Per cent of $C_2H_4O_2$ in liquid mixture.	Mols. $C_2H_4O_2$ in 100 mols. of liquid mixture.	Molecular mass of acetic acid.
10	5.1	161
20	10.5	166
30	16.2	172
40	22.6	177
50	29.6	186
60	37.2	198
70	46.7	208
80	58.7	218
90	75.2	231
100	100.0	244

TABLE XVI.

Molecular Mass of Acetic Acid dissolved in Toluene at 35°.

Per cent of $C_2H_4O_2$ in liquid mixture.	Mols. $C_2H_4O_2$ in 100 mols. of liquid mixture.	Molecular mass of acetic acid.
10	6.1	159
20	12.4	163
30	19.0	168
40	26.5	170
50	32.8	188
60	41.3	196
70	51.2	204
80	61.1	213
90	78.4	228
100	100.0	240

Considering Tables XIV. and XVI. first, we see that the values of x are approximately the same, the molecular mass of the acid becoming less and less as it is more and more diluted with benzene or toluene. It is remarkable that these two series of values for x fall out so nearly the same, for in the mixture of toluene and acetic acid the differences of their vapour-tensions is so slight that the line of partial pressures of toluene is nearly horizontal, and an error of one millimetre in the determination of the partial pressure may occasion an error of four units in the molecular concentration; in the mixture of benzene and

* Abridged from the *Journal of the American Chemical Society*, vol. xvii., No. 8, August, 1895.

acid, however, the error arising from this source is not more than three-tenths of a unit, the angle made by the line of partial pressures being considerably greater than in the case of the other mixture.

For the determination carried out at 20° on the mixture of benzene and acetic acid, it is seen that the number of molecules of acid is less, and hence their molecular mass is greater than when the determinations were carried out at 35°. This is just what is to be expected, for the lowering of temperature has been found to be invariably accompanied by an increase in the condensation of the molecule.

I have sketched the curves corresponding to the values of m and x given in the foregoing tables in a system of co-ordinates with percentage composition as axis of abscissæ and molecular masses as axis of ordinates.

The curves for the mixture of acetic acid and benzene at 35° practically coincides with that of the mixture of acetic acid and toluene at 35°, while the curve for the mixture of benzene and acetic acid at 20° is parallel and slightly above the other two. The curves are perfectly regular in form, and if prolonged to cut the right-hand axis of ordinates cannot give values varying by more than one unit; accordingly it may be claimed that the point where the axis of ordinates is cut by the extrapolated curve gives to about one unit the molecular mass of acetic acid in the liquid state at the temperature taken for the determinations. The results of my extrapolations gives as the molecular mass of liquid acetic acid at 35°, 240, and at 20° 244.

It is interesting to compare these results with those obtained by Ramsay and Shields ("Ueber die Molekulargewichte der Flüssigkeiten," *Zeit. phys. Chem.*, xii., 470, 1893). These investigators found by the determination of the superficial tension of acetic acid that its molecular mass between the temperature limits, 16° and 46°, was equal to $217.2 (60 \times 3.62)$; although this result leaves room for considerable uncertainty as to what the molecular mass of the acid is at any given temperature between these limits, it is in corroboration of my results; for, as has been well established, the degree of association in the molecules of a complex liquid is greater the lower the temperature, and my results pertain to temperatures which are lower or about the same as the mean of the two extreme temperatures given by the two English chemists.

The method of determining the molecular masses of liquids described in this section is the only one as yet devised which permits of the determination at any given temperature of the mass of the molecule.

It is founded on empirical results and depends upon no hypothesis other than the universally recognised one of Avogadro. It is applicable to all cases where the substances under examination can be accurately analysed. It calls for no special apparatus, even a modest laboratory being provided with the necessary pieces. It requires no great amount of manipulative skill, and the results are obtained in relatively short time. I hope that it will be rigidly tested by chemists, and any omissions of this mere sketch be supplied.

Resumé.

The main results of this article may be summed up as follows:—

1. A method of determining the partial pressures of mixtures of liquids has been elaborated, and its sources of error discussed.
2. Although the method can be said to give the vapour-tensions of pure liquids with an accuracy equal to that obtainable by the best of other methods only when the liquids are not very volatile, the results obtained by it for mixtures of liquids of not too different volatilities are accurate enough to serve as the experimental basis for theoretical deductions and generalisations.
3. A number of mixtures of representative liquids have been investigated as regards their vapour-tensions.
4. In some cases extremely simple relations were found; in others, certain complexities presented themselves.

5. A re-calculation of Regnault's determinations of the vapour-tensions of some mixtures of normal liquids, as well as a consideration of Raoult's conclusions and Brown's work on the boiling-points of solutions, showed that it was permissible to apply what was found true for any one temperature to any other.

6. The relations between the concentrations in the gaseous and liquid phases were found to be quite simple and entirely in accordance with the provisions of the relations established by Planck and Nernst.

7. The changes of temperature occurring when certain liquids were mixed were found to be very small, and the resulting mixtures were those which exhibited the simplest relations in their vapour-tensions.

8. The vapour-tensions of mixtures of acetic acid with benzene and with toluene were determined, and the results were such as to permit of the determination of the molecular mass of the dissolved and liquid acid.

9. A general method for the determination of the molecular masses of associated liquids at any given temperature was developed and illustrated with acetic acid.

The experimental part of this investigation was done in a laboratory in the School of Mines at Paris, placed at my disposition by the authorities of that noble institution; and I here take the pleasant privilege of thanking them for the courtesy thus extended to me. My cordial thanks are also due to M. Emilio Damour, Ingénieur Civil des Mines, for his foreseeing kindness in furnishing me with apparatus and material; especially are my thanks due, however, to M. H. Le Chatelier, Ingénieur en Chef des Mines, whose wise direction and good counsel have been of great value to me throughout the work.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 7th, 1895.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

MESSRS. A. F. Fuerst, T. F. H. Gilbard, E. T. Read, and A. Stansfield were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of the Earl of Berkeley, Boars Hill, Abingdon; Messrs. Arthur Jenner Chapman, Burleigh House, Yerbury Road, Upper Holloway; George Bertram Cockburn, B.A., St. George's Hospital, S.W.; Charles Crocker, St. Peter's Road, Cockett, Swansea; Gurney Cuthbertson, 60, Shoreham Street, Sheffield; William Dixon, 102, Spring Street, Bury, Lancs.; Patrick Joseph D. Fielding, 8, St. Joseph's Place, Cork; James Gardner, 80, Heaton Terrace, Middleton, near Manchester; Edward Graham, B.Sc., Dalton Hall, Manchester; Edgar Septimus Hanes, 108, Alexandra Road, St. John's Wood, N.W.; Thomas Hawkins Percy Heriot, 23, Wolseley Road, Crouch End, N.; Frederick Arthur Hillard, B.A., 1, Upper Tichborne Street, Leicester; Arthur Edward Holme, M.A., 3, Ash Terrace, Savile Town, Dewsbury; Alfred James, 18, St. Andrew's Drive, Pollokshields, N.B.; Frederick Edward Johnson, 16, Stanley Terrace, West Park, Hull; Leonard P. Kinnicutt, Ph.D., &c., Worcester, Mass., U.S.A.; Walter Mansfield, Trafalgar House, Broughton, Lancs.; Cecil Massey, Lyndon House, Lenton Boulevard, Nottingham; James McCreath, 4, Lombard Court, E.C.; David James Morgan, 10, Northampton Place, Swansea; Herbert Peck, Wigan Road, Ormskirk; William Round, 45, St. Peter's Road, Handsworth, Birmingham; Clarence Arthur Seyler, B.Sc., 31, Windsor Terrace, Swansea; Matthew Smith, B.A., Aston Hall, Preston Brook, Cheshire; Frank Robert Stephens, Idris and Co., Camden Town, N.W.; George Stone, Sydney, N.S.W.; Albert

Thorpe, Charnwood House, Sleaford Road, Preston; John Williams, B.A., Wesley College, Sheffield; Thomas Rowland Wingfield, 43, Dorset Street, Bolton; William Chattaway, Apothecaries Hall, Blackfriars, E.C.; Martin Priest, Apothecaries Hall, Blackfriars, E.C.; William Oakes Kibble, Norton Villa, Buckhurst Hill, Essex.

The PRESIDENT announced that the following telegram had been sent to Madame Pasteur on the death of her husband, M. Louis Pasteur, in October last:—

"Madame Pasteur, Institut Pasteur, Rue Dutot, Paris. The Chemical Society of London, in common with the entire scientific world, mourns the loss of its illustrious Foreign Member, and begs to express to you its deepest sympathy.

"VERNON HARCOURT, *President*,
"T. E. THORPE, *Treasurer*.
"JOHN M. THOMSON,
"WYNDHAM R. DUNSTAN, } *Secretaries*,
"R. MELDOLA,

and that the following Address had been presented on behalf of the Society by Dr. Frankland to the Institute of France on the occasion of its Hundredth Anniversary:—

"The leading men of the French nation in Literature, Science, and Art celebrate to-day the hundredth anniversary of a great event. There had perished in the throes of the revolution a group of Academies which for more than a hundred years had shed lustre upon France, and had contributed among the foremost to the general advance of mankind. It was an eclipse of which the darkness could not last long. Two years later, on the 25th of October, 1795, the law was passed which revived the Academies and combined them in the Institute.

"The Chemical Society of London, born half a century later, and representing one of the sciences which are united under the Académie des Sciences Mathématiques et Physiques, desire on this occasion to record their sense of the splendid additions to chemical knowledge and thought which have been made by members of the French Academy. They respectfully offer to the Institute their congratulations on what has been achieved, to which they must now add their sympathy and regret for those who have passed away, thinking especially of the recent loss which science and humanity have sustained by the death of the illustrious Pasteur.

"*President*, A. VERNON HARCOURT.
"*Treasurer*, T. E. THORPE.
"*Honorary Secretaries*, { JOHN M. THOMSON.
WYNDHAM R. DUNSTAN.
"*Foreign Secretary*, RAPHAEL MELDOLA."

October 25th, 1895.

Of the following papers those marked * were read:—

*120. "On Flame Temperatures and the Acetylene Theory of Luminosity. By ARTHUR SMITHELLS, B.Sc.

The author has submitted to experimental and critical examination the acetylene theory of luminous hydrocarbon flames advocated by Lewes (*Trans. Chem. Soc.*, 1895, lxi., 322; *Proc. Roy. Soc.*, 1895, lvii., 450), and concludes that it is untenable.

Details of the measurement of the temperatures of different parts of hydrocarbon flames by means of the Le Chatelier thermo-couple are given. It is shown that, to obtain readings of any value, the wires constituting the couple must be bent so as to fit the particular region of the flame in which the measurement is desired, and that if the sheet of flame be thin even this precaution is insufficient. The exploration of an ordinary flat coal-gas flame gives evidence of no sudden change of temperature in a vertical plane. Sudden changes are found, however, when the couple is moved from the middle of the flame outwards in a horizontal plane, and the mantle has a temperature higher than the melting-point of platinum.

The author considers Lewes's description of the distribution of zones in flames to be based on erroneous tem-

perature measurements, and finds no evidence of such a local condition of temperature as would point to the decomposition of acetylene. The conclusion in favour of the acetylene theory, based on the comparative luminosity of the ethylene and acetylene flames, is attributed to neglect of the consideration that in the latter there is a higher temperature and a greater relative amount of carbon. The indirect evidence derived from the behaviour of cyanogen is stated to arise from the yellow ammonia flame having been mistaken for one containing solid carbon. The theoretical arguments based on thermo-chemical considerations are adversely criticised.

The author maintains that the luminosity of hydrocarbon flames, including the flame of acetylene, can be adequately explained on the older theory of their structure confirmed and extended by his earlier experiments (*Trans. Chem. Soc.*, 1892, lxi., 217). According to this view, a luminous flame is invested by a sheath of gas in non-luminous combustion. This sheath, which is double at the lower part, corresponds to the two cones of a Bunsen flame, and produces an exceedingly high temperature. The gas within this sheath is intensely heated as it ascends, and is gradually decomposed so as to furnish a sheet of carbon particles, becoming more and more numerous. These glow partly by heat and partly by combustion; the higher the temperature of the non-luminous sheath, and the greater the relative number of particles, the brighter will be the flame. This is well seen in the case of acetylene. The author believes that the precise steps in the decomposition of a hydrocarbon by which carbon is deposited are at present unascertainable by any direct means, but, as the glow of the carbon particles in a hydrocarbon flame is in no case greater than that acquired by a platinum wire immersed in the same region, he considers that there is no ground for supposing that the endothermic decomposition of acetylene (of which substance only a very small quantity has been found in the flame gases) plays any appreciable part in the phenomenon.

*121. "A New Series of Hydrazines." By FREDERICK D. CHATTAWAY and HARRY INGLE, B.Sc.

Primary and secondary hydrazines have proved such important substances that other substituted derivatives of hydrazine have scarcely been studied.

Theoretically, hydrazine should yield five series of substituted derivatives, of which only three are known, the primary, the secondary symmetrical, and the secondary unsymmetrical. No simple method of obtaining members of the other series has hitherto been described, and the authors have undertaken their investigation.

The quaternary hydrazines, which are dealt with in the paper, can be obtained by a simple general reaction from the secondary amines.

The secondary amine is treated with sodium or sodium ethylate, whereby the hydrogen atom is replaced by sodium, $R_2NH + Na = R_2NNa + H$. The equivalent quantity of iodine is then allowed to act upon the sodium compound, when the sodium atoms are withdrawn, and the two substituted amido-groups unite to form the quaternary hydrazine,—



The aromatic quaternary hydrazines which have been so far more especially studied are stable well-crystallised compounds, which are not easily oxidised, and are scarcely, if at all, basic. Their percentage composition, and the molecular weights obtained by Raoult's method, using benzene as a solvent, agree well with the theoretical.

Tetraphenyl hydrazine, $(C_6H_5)_2N \cdot N(C_6H_5)_2$, obtained by the above reaction from diphenylamine, crystallises in long orthorhombic prisms, m. p. 147°. It is easily soluble in benzene, chloroform, and acetone, and dissolves in cold concentrated sulphuric acid, giving a deep purple solution.

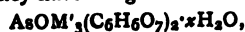
Tetra-p-tolyl hydrazine, $(C_6H_4CH_3)_2N \cdot N(C_6H_4CH_3)_2$,

prepared from di-*p*-tolylamine, crystallises in large pale yellow monoclinic prisms or tables, m.p. 138°. It is easily soluble in benzene, acetone, and chloroform, and dissolves in cold concentrated sulphuric acid, giving a brilliant azure-blue solution.

122. "*The Action of certain Acidic Oxides on Salts of Hydroxy-acids.* (Part II.). By G. G. HENDERSON, D.Sc., M.A., and DAVID PRENTICE.

The action of antimonious and arsenious oxides upon salts of citric, malic, lactic, and mucic acids has been studied, and several new salts have been prepared, the oxide being heated with solutions of salts of those acids for varying periods, and the compounds formed precipitated by alcohol or separated by crystallisation.

With citrates of potassium, sodium, and ammonium, antimonious oxide gave compounds of the general formula $\text{SbOM}'_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot x\text{H}_2\text{O}$, which are all crystalline and readily soluble in water. A sparingly soluble barium salt, $\text{SbOBA}_2(\text{C}_6\text{H}_5\text{O}_7)_3 \cdot 10\text{H}_2\text{O}$, was obtained by precipitation, and from it a very soluble crystalline compound of the probable formula $\text{OH}'\text{Sb}:(\text{C}_6\text{H}_7\text{O}_7)_2$ was prepared. Arsenious oxide gave similar compounds with citrates of the alkalis. They have the general formula—



are crystalline, and dissolve freely in water.

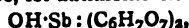
Both antimonious and arsenious oxides dissolve in boiling aqueous solutions of alkaline malates. A well-crystallised antimony compound, whose simplest formula is $(\text{SbO})_3\text{K}_4\text{H}(\text{C}_4\text{H}_5\text{O}_5)_6 \cdot 3\text{H}_2\text{O}$, was prepared, but no corresponding arsenic compounds have yet been obtained, owing to their instability.

Boiling solutions of lactates of the alkalis and of barium readily dissolve both antimonious and arsenious oxides, and alcohol precipitates colourless syrups, containing large quantities of unaltered lactates.

Compounds of the oxides with mucates were also prepared, though with some difficulty. Two antimony compounds of the formulæ—

$2\text{SbOKC}_6\text{H}_5\text{O}_8 \cdot \text{KC}_6\text{H}_5\text{O}_8 \cdot 6\text{H}_2\text{O}$ and $\text{SbOKC}_6\text{H}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$ were obtained in the form of sparingly soluble crystalline powders. An arsenic compound corresponding to the second of these was likewise obtained.

These substances might be regarded as double citrates, malates, &c., containing the radicles $(\text{SbO})'$ and $(\text{AsO})'$, but, if so, then in all probability those radicles replace the hydrogen of alcoholic hydroxyl groups, and not the hydrogen of carboxyl groups as in the formation of salts, for otherwise it is difficult to understand why hydroxy-acids alone seem to have the power of forming such compounds. On the other hand, they might be regarded as salts of acids derived from antimonious or arsenious acids by replacement of two of the hydroxyl groups of those acids by organic acid radicles, as is the case with the antimonio- and arsenio-tartrates. The formulæ of such acids would be, for antimonio-citric acid—



for antimonio-malic acid $\text{OH}'\text{Sb}:(\text{C}_4\text{H}_5\text{O}_5)_2$, for antimonio-mucic acid $\text{OH}'\text{Sb}:\text{C}_6\text{H}_5\text{O}_8$; the formulæ of the arsenious acid derivatives would be similar to these. In the case of some at least of the new compounds this view appears preferable.

123. "*Sodium Nitrososulphate.*" By E. DIVERS F.R.S., and T. HAGA.

Sodium nitrososulphate, being a very soluble salt, does not crystallise out when even the strongest solution of sodium sulphite is treated with nitric oxide. But if the solution, after this treatment has been continued long enough, be deprived of most of its sodium sulphate by freezing out, and be then evaporated in a vacuum to a very small volume, sodium nitrososulphate is deposited in crystals.

It is an anhydrous salt, forming very minute crystals, which in the solution adhere together in opaque crusts.

The salt is slightly alkaline to litmus, and tastes very much like common salt. It is exceedingly soluble in water and very unstable, wet or dry. In the dry state, in which it can be obtained in a desiccator, and at the common temperature, it rapidly decomposes on exposure to (damp) air, becomes nearly as hot as slaking lime, and gives off large quantities of nitrous and nitric oxides. The residue consists of sodium sulphate and sulphite. It thus behaves at the common temperature as potassium nitrososulphate only does when heated to about 100°.

In solution in water it continuously decomposes, like the potassium salt, into sulphate and nitrous oxide. A little sodium hydroxide greatly retards this decomposition in water, but if a solution of the salt containing sodium hydroxide is heated to boiling, the salt decomposes freely into nitric oxide and sulphite. This behaviour is unlike that of the potassium salt.

Its composition, which was indirectly determined quantitatively, is $\text{Na}:\text{ON}:\text{NO}:\text{SO}_3\text{Na}$.

124. "*The Constitution of Nitrososulphates.*" By E. DIVERS, F.R.S., and T. HAGA.

Potassium nitrososulphate in aqueous solution becomes strongly alkaline when mixed with a little alcohol. This is due to the salt and the alcohol partly decomposing into potassium ethyl sulphate, nitrous oxide, and potassium hydroxide. The primary reaction is, beyond a doubt, one in which potassium hydrogen hyponitrite is produced, along with the potassium ethyl sulphate, although none can be detected; but then its formation proceeds here very slowly, and certainly not faster than it is known to decompose of itself into potassium hydroxide and nitrous oxide.

This reaction is peculiarly interesting, for in it alcohol decomposes a sulphate in alkaline solution, and liberates potassium hydroxide, though indirectly. The occurrence of this reaction, taken with other properties, solves the problem of the constitution of the nitrososulphates. They are anhydro-double salts of hyponitrous and sulphuric acids, which hydrolyse into the acid salts of these acids, the acid salts simultaneously changing into normal sulphate, nitrous oxide, and water. They are analogous to the thiosulphates, the hyponitrite radicle acting as sulphur does in them. Thus we see calcium thiosulphate and sodium nitrososulphate forming themselves from the sulphite of their metal and decomposing into it again, under precisely similar conditions. Nitrososulphates are, however, true sulphates, as their reactions with alcohol and with acidified barium chloride show, their nitrogen being united to their sulphur only though an atom of oxygen, $\text{KON}_2\text{O} \cdot \text{SO}_3\text{K}$.

(To be continued).

PHYSICAL SOCIETY.

Special Meeting, November 22nd, 1895.

Captain W. DE W. ABNEY, President, in the Chair.

THE following resolution with reference to the Articles of Association was passed:—

"In Article 33 to strike out the words 'by the payment of £10 in one sum,' and in place of this to insert the words 'the composition fee shall be for every member who shall not have paid ten annual subscriptions, fifteen times the amount of the annual subscription payable by such member; and for any member who shall have already paid ten or more annual subscriptions, ten times the amount of the annual subscription payable by such member.'"

The Ordinary Meeting then took place.

Dr. G. JOHNSTONE STONEY exhibited a Print of Profs. Runge and Paschen's Photograph of the Spectrum of the Gas obtained from Clèveite, together with a Diagram

illustrating the Manner in which these Observers have arranged all the Lines obtained in two Sets, each Set containing Three Series of Lines.

Dr. STONEY also drew attention to the resemblance between each of these sets of three series of lines and the similar triple series obtained in the case of the metals of Mendeleeff's first group. The lines of the different series in the case of the gas obtained from clèveite have certain definite peculiarities, which permit of their identification and selection. The two gases, to the presence of which the two sets of lines are presumably due, can be partly separated by diffusion through a plug of asbestos. Prof. Ramsay's observation that by suitably altering the pressure of the gas the predominance of the lines in either of the two sets can be increased is, however, against the theory that the two gases are really separated by diffusion.

Three of the original negatives taken by Prof. Rowland when preparing his map of the solar spectrum were also exhibited.

Dr. GLADSTONE said he had examined the spectrum of the gas in two tubes, one of which had been filled by diffusion through an asbestos plug, and the helium line (D_3) was certainly brighter in one tube than in the other, though the brightness of the remaining lines appeared about the same in both tubes. As to the difficulty of allocating the new gases in Mendeleeff's table, it appeared to him (Dr. Gladstone) that they would have to be put in the first group, between hydrogen and lithium. An examination of the successive differences between adjacent members of the metals in the first group showed that these differences increased as we go downward. If, then, the new gases have atomic weights of, say, 2, 4, and 4, we should have for these differences 2, 2, 3, 16, 16, 26, &c., instead of 6, 16, 16, &c., as at present. The important point which required investigation was whether these two gases were really simple bodies or not.

Prof. SILVANUS THOMPSON asked if Runge and Paschen had performed a similar analysis of the lines in the spectra of other elements besides the members of the first group. He would also like to know if, in the case of any element besides hydrogen, the lines could be arranged in a single series.

Dr. STONEY, in reply, said that the spectra of most of the metals had been analysed; the chief exceptions being iron, nickel, cobalt, and manganese. There was no other element besides hydrogen which gave a single series of lines.

Prof. HERSCHEL gave an account of a line of reasoning which had led him many years ago to a formula resembling that expressing Balmer's law for the hydrogen lines, namely,—

$$\frac{1}{\lambda} = 1 - \frac{4}{n^2}.$$

The Chairman (Captain ABNEY) drew attention to the fact that Runge expressed his results to $\frac{1}{10000}$ th of an Angström unit, although Dr. Stoney had said the measurements could only be made to within $\frac{1}{100}$ th of a unit. There was great lack of uniformity in the method of drawing spectra in general use; he strongly recommended the placing of the red end of the spectrum to the right, so that the wave-lengths increased from left to right. As to the three series of lines obtained in the case of most elements, it was not conclusively proved that they were not due in each case to three distinct kinds of molecules, and it will probably be found that there are more than two simple gases present in the gas evolved from clèveite.

Mr. R. APPLEYARD read a "Notes on the Action of Sulphur Vapour on Copper."

When a copper wire is exposed for some time to the action of sulphur vapour it becomes entirely converted to sulphide of copper, and it is found that there is a fine axial hole running down the rod of sulphide formed. Rods of copper of square section, cut from a block of copper after exposure to the action of sulphur vapour, also

exhibited the axial hole, the rod of sulphide formed being of circular cross-section. In every case the diameter of the rod of sulphide formed is about twice that of the original rod of copper. Delta metal was found to be unaffected upon by the sulphur vapour.

Mr. APPLEYARD then read a paper on "A 'Direct-reading' Platinum Thermometer."

This form of platinum thermometer has been devised with the view of determining the temperature of the dielectrics employed in some experiments on the variation of the electrical resistance of dielectrics with temperature. The thermometers consist of six platinum coils, each of about 7 ohms resistance, attached to thick copper leads. A slide-wire Wheatstone's bridge is employed to measure the resistance. The stretched wire is 3 metres long, and the moving contact so arranged that it is impossible to damage the wire. The auxiliary coils used in connection with the bridge are immersed in a bath of paraffin oil, the temperature of which is maintained constant, and a little above that of the air, by means of a glow-lamp immersed in the oil.

Mr. APPLEYARD also read "A Historical Note on Resistance and its Change with Temperature."

He showed that the earliest measurements of the variation of resistance with temperature were made by Lentz in 1833. Some experiments on this subject made by Davy were also referred to, and some of these experiments repeated before the Society.

Mr. TROTTER said he agreed with the author that the "reserve of precision" at our disposal, on account of the delicacy of some of our modern instruments, ought to be made use of to facilitate the rapid performance of many measurements where the utmost accuracy is not necessary. He had the impression that platinum silver was not now considered the best material for use as the bridge wire.

Mr. H. F. BURSTALL explained the differences between the temperature as measured on the mercury, air, and platinum thermometers. At a temperature of about 40° the platinum thermometer read about 0.4°, and the mercury thermometer about 0.1° below the air thermometer. Prof. Callendar had obtained measurements of temperature correct to within 0.1° by using a Weston voltmeter and an ordinary Wheatstone bridge; the variations of resistance, and hence the temperature, being read directly from the deflections on the voltmeter.

Mr. RHODES thought that, except where extreme accuracy was necessary, the mercury thermometer was very much more convenient than the platinum thermometer.

Mr. BURSTALL said the great convenience of the platinum thermometer lay in the fact that the scale could be read at a distance of many yards from the point where the temperature was being measured, and hence could be used in many places where it would be impossible to read a mercury thermometer.

Mr. BLAKESLEY considered that the author was somewhat bold to state that for general purposes it was never necessary to measure temperature to nearer than one-tenth of a degree.

The author having replied, the Society adjourned till December 13th.

Appointment.—Mr. W. Lincoln Sutton, A.I.C., has been appointed Public Analyst for the city of Norwich.

Pasteur's Successors.—According to the *Chemiker Zeitung* a dispute has arisen in the Pasteur Institute as to the succession to the presidency of this establishment, Duclaux or Roux. Duclaux ranks high in the scientific world, whilst Roux figures as a physician. The Council of the Institute finally decided in favour of Duclaux, whilst Roux is appointed Second Director. It is not generally known that Pasteur, in addition to his scientific eminence, was distinguished as a financier.

NOTICES OF BOOKS.

A Treatise on the Manufacture of Soap and Candles, Lubricants, and Glycerin. By WM. LANT CARPENTER, B.A., B.Sc., F.C.S., &c. Second Edition, Revised and Enlarged by HENRY LEASK. London: E. and F. N. Spon. New York: Spon and Chamberlain. 1895. Crown 8vo., pp. 446.

It is satisfactory to find that this work has not undergone any deterioration from the regretted death of its author. The second edition, now before us, has been entrusted to Mr. Henry Leask, a recognised authority on paraffin refining and on the manufacture of candles.

In the first chapter we are rightly told that though soap was in use prior to the Christian Era, yet the modern development of the soap manufacture dates only from the early part of the present century, and is substantially due to two French inventors, Chevreul and Leblanc.

We regret the recent decline in the consumption of palm-oil, since in vegetable fats we are substantially safe from the presence of the morbid products of microscopic life. The author refers to the liability of coconut-oil and palm-oil to turn rancid. We once knew of a cask of the latter oil reaching the consumer, in Yorkshire, perfectly free from rancidity. This was practically no advantage, since the greater part was eaten by the workmen. Concerning linseed oil, the author mentions a fraud practised in the Russian ports, viz., the addition of 1 measure of hemp seed to every 39, or latterly 19, measures of linseed. In India the oil seeds are often grown promiscuously. Indeed to obtain absolutely pure oils for any scientific purpose is a difficult and doubtful matter.

The vegetable tallows, the products of species of *Hopsea*, and of *Stillingia salifera*, are found, as lubricants, superior even to olive oil.

The following remark is gravely significant:—"The soap-pan appears to be the natural destination of any rough fat-containing matter which can be turned to no other purpose."

It is interesting that large quantities of Fuller's earth are yet exported from this country to America to serve in the purification of lard. The bleaching of oils and fats still offers scope to the inventor, since many agents which decolourise at the same time promote rancidity.

The problem of recovering glycerin from spent lyes is rightly pronounced very difficult, and it is regarded as probable that in the future all glycerin will be obtained directly from fats prior to saponification.

The difficulty of correct sampling solid and semi-solid fats is insisted upon. The identification of oils in mixtures—and there are few samples which may not be regarded as mixtures—is discussed at some length. The spectroscopy assists us only in some cases. Maumené's test, according to Allen, sometimes gives unaccountable results.

When soap-makers manufacture their own alkali, their operations are much complicated, and require more plant and space; hence whether such causticising is economical or not must depend on local conditions. The Solvay alkali process will not, it is considered, commend itself to the adoption of soap-boilers, though the ammonia-soda is excellent. It is to be regretted that in the English alkali trade the false atomic weight 24 is still used instead of 23, the correct figure. We may here regret the countenance given to Baumé's hydrometer in this work, though two pages are given up to its inconsistencies (pp. 278 and 279).

The common opinion that a soap-work is necessarily a public nuisance is totally erroneous. Such an establishment, if well-conducted, is far less offensive than, e.g., a fried-fish shop.

Space will not allow us to extend our notice of this book to the remaining portions, which treat of lubricants

and of the manufacture of candles. Upon the whole, this second edition may be regarded as an improvement upon its predecessor. It will be found a useful manual by the student of those departments of technical chemistry which discuss the applications of the oils and fats.

Perken, Son, and Rayment's Illustrated Catalogue of Photographic Apparatus, Magic Lanterns, and Optical Instruments: contains numerous Reductions in Prices, many Novelties, and Fresh Matter. "Optimus," 99, Hatton Garden, Holborn Viaduct, and 141, Oxford Street, W., London.

THE photographer, be he professional or amateur, will find here ample scope for choice of cameras and all other fittings and accessories. The lanterns shown are a great convenience for scientific lecturers, as well as for their hearers.

The old "sketching lecture," in which an awkward representation of apparatus, of specimens, or dissections, was given by dint of chalk and black-board, is evidently and deservedly fading into the "infinite azure," whilst the lecturer can, by means of the lantern and of appropriate slides, give a far clearer and more accurate view of the objects to be explained.

The catalogue before us gives a wonderful assortment of slides, suitable for illustrating all kinds of lectures, astronomical, historical, geological, antiquarian, biological, and miscellaneous.

In this catalogue, as we believe in all others issued by opticians, we notice that the spectroscope does not figure prominently, if at all. This is a proof that an instrument so necessary for research in various sciences is very rarely, as yet, in demand by investigators.

CORRESPONDENCE.

PRODUCTION OF CITRIC ACID BY THE
OXIDATION OF CANE-SUGAR.

To the Editor of the Chemical News.

SIR,—We certainly "profess to have repeated" Dr. Phipson's experiments, and have taken care to follow his instructions implicitly. We fail to see why he should state that we have not done so.

Dr. Phipson now says that the products of oxidation of cane-sugar by permanganate vary considerably, "according to the respective quantities of permanganic acid and sugar, according as sulphuric acid or nitric acid is used, and according to the temperature of the day." We have employed the reagents in the proportions Dr. Phipson recommended, and have failed to produce any citric acid, as we also did on previous occasions when we used our own discretion as to the proportions of the materials.

If Dr. Phipson will tell us any better way of recognising citric acid in a liquid also containing tartaric acid, saccharic acid, and formic acid, than that based on the precipitation of calcium citrate by boiling a neutral solution, we shall be glad to try his process. We confess that we do not know any better plan.

Dr. Phipson, in conclusion, asks us what becomes of the sugar, if saccharic acid, tartaric acid, formic acid, and citric acid are not formed. Saccharic acid is well known to be a product of the oxidation of cane-sugar, and tartaric acid, we have reason to believe, can be obtained under suitable conditions. The question of formic acid is open. It is for Dr. Phipson to prove that citric acid is formed, as asserted by him, and to prescribe a method by which other chemists can repeat his experiments successfully.—We are, &c.,

ALFRED B. SEARLE,
ARNOLD R. TANKARD.

67, Surrey Street, Sheffield,
November 23, 1895.

CHEMICAL EDUCATION.

To the Editor of the Chemical News.

SIR,—In your "Address to Students" in the number last to hand (CHEMICAL NEWS, vol. lxxii., p. 111), you refer to the chemical education obtainable and appreciated, and therefore paid for, in Germany. I have seen the same matter often written of for some years, and the want of progress in chemical industries in Great Britain ascribed to the want of appreciation of such trained skill, by British manufacturers. It is always advantageous to trace things to their first cause; and I think that in this case it may be found in a remark made to me in the early sixties by Dr. E. Ronalds, then in Edinburgh. I had formerly been his assistant, he being managing partner in the Bonnington Chemical Works, where the tar from Edinburgh and Leith was treated, and I made some mauve from aniline in a fractionated series of coal-tar bases shortly after Perkins patented his process—about 1857, I think—and on the occasion referred to, whilst speaking of the coal-tar colours, he said:—"The Excise will drive the business out of the country, so there is no use touching it."

Actually this is what has happened, as the Government by the duty on alcohol, and the rigorous regulations as to its use, have driven a trade worth £20,000,000 per annum out of Great Britain. For the greater part of the thirty-eight years since the industry began, the greater portion of the raw material was provided by the United Kingdom, and all the first colours were discovered and made there, showing that the chemical knowledge was there. The use of free alcohol then transferred the manufacture to Germany. The manufacturer demanded technical chemists; and technical chemical schools arose, not only supplying the demand, but leaving a surplus of trained men which has overflowed into every branch of chemical industry. And now the supply of the raw material for that manufacture is curtailed to the United Kingdom, in consequence of German improvements in coke making, so that benzine, which used to be 15/- per gallon, is now 1/-.

In the first half of this century the great strides in industrial chemistry were made in bleaching and light production, and that in the United Kingdom; and that as the Government did not interfere with them they took root and flourished. In the second half of the century, the great stride has been in colours; but here the Government insisted on its pound of flesh, so this industry fled, and, in consequence, other British chemical manufactures are threatened.

To support technical schools there must be a demand for those trained in them, and good positions in view; and this can only come from a rapidly growing industry in which a few have drawn prizes and hundreds think they may do the same. Other industries which have arrived at the rule-of-thumb stage are benefited only indirectly, and it must be remembered that what is the highly scientific to-day becomes the rule-of-thumb of a few years hence.—I am, &c.,

W. A. D.

Sydney, October 21, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxi., No. 19, November 4, 1895.

Action of Silicon upon Iron, Chromium, and Silver.—H. Moissan.—This paper will be inserted in full.

Spectral Researches on the Star Altair (α -Aquilæ).—H. Deslandres.—The bulk of this memoir is purely

astronomical, but it may be here mentioned that, unlike the other white stars, Altair has iron and calcium rays almost as broad as the rays of hydrogen. They have been detected on seeking for, among the broad black rays of the spectrum, the small brilliant reversed rays which constitute the bulk of the atmospheric spectrum.

Treatment of the Emerald and the Preparation of Pure Glucina.—P. Lebeau.—This memoir will be inserted in full.

On a Group of Mineral Waters containing Ammonia; Bituminous Waters.—F. Parmentier.—The waters in question are obtained from springs in the neighbourhood of Clermont. Ammonia can be detected in them by means of the Nessler reagent. Beyond bituminous matter, recognisable by the smell and taste, there is no other organic matter.

Determination of Tannin in Wines.—E. Manceau.—The author's method is as follows:—About 100 c.c. of wine are placed in a small flask with a ground glass stopper, and 1 grm. of gut-string. In a week, at about 15°, all the tannin will have been taken up. He then titrates with a solution of permanganate, 1 c.c. of which corresponds to 0.2 m.grm. of pure gallo-tannin, using as indicator a sulphuric solution of indigotin. The difference of the volumes of permanganate taken to decolourise 25 c.c. of the original wine and 25 c.c. of the same wine deprived of tannin shows the weight of gallotannin corresponding to 25 c.c. of the wine. To prepare the gut-strings, violin strings (not oiled) are submitted in succession to prolonged washing in alcoholised water, acidulated water, and pure water, until they no longer yielded to these solvents any substance capable of reducing permanganate in the cold.

Action of Chlorine upon Normal Propylic Alcohol.—André Brochet.—The author has made an especial study of α -chloropropionic aldehyd and of chlorodipropylacetal.

Ozotoluene.—Adolphe Renard.—If pure toluene is submitted to the action of ozone, there is formed an explosive product, ozotoluene, analogous to oxobenzene. It forms a white translucent mass, of a gelatinous aspect. It decomposes at from 8° to 10°. Its composition is probably $C_7H_5O_6$, whence it is the higher homologue of oxobenzene, $C_6H_5O_6$. With pure xylene (ortho-xylene) submitted to ozone at 0° there is also obtained a white explosive product.

Study of the Nitration of Menthone.—M. Konavloff.—The author has obtained a product of the composition $C_{16}H_{17}(NO_2)O$.

Fermentation of Cellulose.—V. Omelianski.—This phenomenon has generally been ascribed to the action of *Bacillus amylobacter*. This organism the author regards as a "collective species." The pure bacillus he considers to be slender, consisting of straight and sinuous joints, from 6 to 7 μ in length and 0.2 to 0.3 μ in breadth. It forms regular round spores.

Experiments on the Direct Production of Pure Ethylic Alcohol by the Fermentation of *Asphodelus ramosus* and *Scilla maritima* by the Aid of Pure Wine Ferments.—G. Rivière and M. Bailhache.—The nature of this paper appears sufficiently from the title.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. x., No. 117.

The Expansion of Glass, and on Soldered Glasses.—A Report presented by Dr. Schott.—For siliceous glasses the expansion increases with the proportion of alkali. Boric acid produces a striking decrease of expansion. In superposing upon each other two glasses of different compositions, it is requisite that there should exist a certain relation between the relative thickness of the two layers of glass and their coefficients of expansion. Thus at Jena they solder normal thermometer glass, the

coefficient of cubic expansion of which between 0° and $100^{\circ} = 0.0000244$, to an aluminous sodium borosilicate the expansion of which = 0.0000177 . The former kind of glass must be placed externally and the second internally in order to form a hollow vessel or a tube. We may also join together three or more layers of two or more glasses. Of two layers of glass with different expansions, after cooling, that with the greatest expansion will be in a state of tension, and the other in a state of compression. External layers in a state of compression increase in a striking manner the resistance of glass to mechanical actions and to rapid changes of temperature. Flasks thus manufactured may be strongly heated (to a temperature of 184°), and may then be sprinkled with cold water without injury. Such glasses are not liable to the sudden rupture presented by glass tempered by the process of De la Bastie.

MEETINGS FOR THE WEEK.

- MONDAY, 2nd.**—Society of Arts, 8. "Mechanical Road Carriages," by H. Worby Beaumont, M. Inst.C.E. (Cantor Lectures).
— Society of Chemical Industry, 8. "Alkali Manufacture by the Hargreaves Bird System of Electrolysis," by Mr. J. Hargreaves, F.C.S. "The Analysis of Chrome Iron Ore, Ferrichrome, and Chrome Steel," by Dr. S. Rideal and Mr. S. Rosenblum.
— Royal Institution, 5. General Monthly Meeting.
- WEDNESDAY, 4th.**—Society of Arts, 8. "Mural Painting with the Aid of Metallic Oxides and Soluble Silicates," by Mrs. Anna Lea-Merritt and Prof. W. C. Roberts-Austen, C.B., F.R.S.
- THURSDAY, 5th.**—Chemical, 8. "The Constitution of Terpenes," by Prof. Armstrong, F.R.S. "New Derivatives from α -Dibromo-camphor," by M. O. Forster. "The Chemistry of Dibromopropylthiocarbimide, and the Action of Bromine and Iodine on Allylthiourea," by Prof. A. E. Dixon. Ballot for the Election of Fellows.

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THE CHEMICAL NEWS.

VOL. LXXII., No. 1880.

ON THE NEW GASES OBTAINED FROM URANINITE.* (SIXTH NOTE).

By J. NORMAN LOCKYER, C.B., F.R.S.

As Mr. Crookes has now published (CHEMICAL NEWS, vol. lxxii., p. 87) the wave-lengths of the lines in the spectra of the new mineral gases observed by him in the tubes supplied by Professor Ramsay, I propose in the present paper to bring together some notes I have made (some of them some time ago) on the same subject.

The researches made at Kensington in connection with the new gases obtained from bröggerite and other minerals has consisted, to a large extent, of comparisons of the lines in their spectra with lines in the spectra of the sun and stars. Preliminary accounts of these comparisons have already been given, and they show that the bright yellow line seen in the gas from bröggerite is by no means the only important one which appears.

Although the general distribution and intensities of the lines in the gases from bröggerite and clèveite sufficiently corresponded with some of the chief "unknown lines" in the solar chromosphere and some of the stars to render identity probable, it was desirable to see how far the conclusion is sustained by detailed investigations of the wave-lengths of the various lines.

The Yellow Line λ 5875'9.—Immediately on receiving from Professor Ramsay, on March 28th, a small bulb of the gas obtained from clèveite, a provisional determination of wave-length was made by Mr. Fowler and myself, in the absence of the sun, by micrometric comparisons with the D lines of sodium, the resulting wave-length being 5876'07 on Rowland's scale. It was at once apparent, therefore, that the gas line was not far removed from the chromospheric D₃, the wave-length of which is given by Rowland as 5875'98.

The bulb being too much blackened by sparking to give sufficient luminosity for further measurements, I set about preparing some of the gas for myself by heating bröggerite *in vacuo*, in the manner I have already described. A new measurement was thus secured on March 30 with a spectroscopic having a dense Jena glass prism of 60°; this gave the wave-length 5876'0.

On April 5th, I attempted to make a direct comparison with the chromospheric line, but though the lines were shown to be excessively near to each other, the observations were not regarded as final.

Professor Ramsay having been kind enough to furnish me, on May 1, with a vacuum tube which showed the yellow line very brilliantly, a further comparison with the chromosphere was made on May 4. The observations were made by Mr. Fowler, in the third order spectrum of a grating having 14438 lines to the inch, and the observing telescope was fitted with a high-power micrometer eye-piece; the dispersion was sufficient to easily show the difference of position of the D₃ line on the east and west limbs, due to the sun's rotation. Observations of the chromosphere were therefore confined to the poles.

During the short time that the tube retained its great brilliancy, a faint line, a little less refrangible than the bright yellow one, and making a close double with it, was readily seen, but afterwards a sudden change took place, and the lines almost faded away. While the gas line was brilliant, it was found to be "the least trace more

refrangible than D₃, about the thickness of the line itself, which was but narrow" (Observatory Note-book"). The sudden diminution in the brightness of the lines made subsequent observations less certain, but the instrumental conditions being slightly varied, it was thought that the gas line was probably less refrangible than the D₃ line by about the same amount that the first observation showed it to be more refrangible. Giving the observations equal weight, the gas line would thus appear to be probably coincident with the middle of the chromospheric line, but if extra weight be given to the first observation, made under much more favourable conditions, the gas line would be slightly more refrangible than the middle of the chromosphere line.

Pressure of other work did not permit the continuation of the comparisons. In the meantime, Runge and Paschen announced (*Nature*, vol. lli., p. 128) that they also had seen the yellow line of the clèveite gas to be a close double, neither component having exactly the same wave-length as D₃, according to Rowland.

They give the wave-length of the brightest component as 5878'883, and the distance apart of the lines as 0'323.

This independent confirmation of the duplicity of the gas line led me to carefully re-observe the D₃ line in the chromosphere for evidences of doubling. On June 14, observations were made by Mr. Shackleton and myself of the D₃ line in the 3rd and 4th order spectra under favourable conditions; "the line was seen best in the 4th order, on an extension of the chromosphere or prominence on the north-east limb of the sun. The D₃ line was seen very well, having every appearance of being double, with a faint component on the red side, dimming away gradually; the line of demarcation between the components was not well marked, but it was seen better in the prominence than anywhere else on the limb." ("Observatory Note-book").

It became clear, then, that the middle of the chromosphere line, as ordinarily seen, and as taken in the comparison of May 4, does not represent the place of the brightest component of the double line, so that exact coincidence was not to be expected.

Though the observations are not yet quite completed, the circumstance that the line is double in both gas and chromosphere spectrum, in each the less refrangible component being the fainter, taken in conjunction with the direct comparisons which have been made, render it highly probable that one of the gases obtained from clèveite is identical with that which produces the D₃ line in the spectrum of the chromosphere.

Other observers have since succeeded in resolving the chromospheric line. On June 20, Professor Hale found the line to be clearly double in the spectrum of a prominence, the less refrangible component being the fainter, and the distance apart of the lines being measured as 0'357 tenth-metres (*Ast. Nach.*, 3302).

The doubling was noted with much less distinctness in the spectrum of the chromosphere itself on June 24. Professor Hale points out that Rowland's value of the wave-length (as well as that of 5875'924, determined by himself on June 19 and 20) does not take account of the fact that the line is a close double.

Dr. Huggins, after some failures, observed the D₃ line to be double on July 10 (*Ast. Nach.*, 3302); he also notes that the less refrangible component was the fainter, and that the distance apart of the lines was about the same as that of the lines in the gas from clèveite, according to Runge and Paschen.

It may be added, that in addition to appearing in the chromosphere, the D₃ line has been observed as a bright line in nebulae by Dr. Copeland, Professor Keeler, and others; in β Lyræ and other bright line stars; and as a dark line in such stars as Bellatrix, by Mr. Fowler, Professor Campbell, and Professor Keeler. In all these cases it is associated with other lines, which, as I shall show presently, are associated with it in the spectra of the new gases.

* A Paper read before the Royal Society, November 21, 1895.

Wave-length (Rowland).	Wave-length (Angström).	Chromosphere (Young). Frequency.	Eclipses 1893. Max. intens.=10. λ R.	Orion nebula. Max. intens.=6. λ R.	Bellatrix. Max. intens.=6. λ R.	Crookes's measures. λ R.
7065.5	7064.0	100	..	..	..	7065.5
6678.3	6676.9	25	..	..	..	6678.1
6371.6	6370.5	5				
6347.3	6346.2	10				
6141.9	6140.6	15				
6122.43	6121.43	5				
6065.7	6064.5	5				
5991.6	5990.0	15				
5875.9	5874.9	100	5876.0	5876.0	5876.0	5876.0
5429.9	5428.8	8				
5404.1	5403.1	5				
5048.2	5047.8	2				
5015.8	5015.0	30	5016.0(4)	..	5016.0(1)	5047.1
4922.3	4921.3	30	4922.0(4)	4924(3)	4922.0(2)	5015.9
4713.4	4712.5	2	4713.2(5)	4716(2)	4715.0(3)	4922.6
4471.8	4471.2	100	4471.8(10)	4472(4)	4472.0(6)	4713.4
4389.5	4388.5	1	4390.0(1)	4390(2)	4389.0(5)	4471.5
4026.5	4025.9	*	4026.0(6)	4026(3)	4026.0(6)	4386.3
3964.0	3963.5	—	3963.8	..	3964.0(3)	4026.1
3888.7	3888.0	—	probable†	..	probable	3964.8
						3888.5

* Professor Young has recently called attention to the fact that although this line was not included in his chromospheric list, he observed and published it in 1883; its frequency is about 15. (*Nature*, vol. lli., p. 458).

† This line is too close to a hydrogen line to enable a definite statement to be made.

The Blue Line, λ 4471.8.—A provisional determination on April 2 of the wave-length of a bright blue line, seen in the spectrum of the gases obtained from a specimen of clèveite, showed that it approximated very closely to a chromospheric line, the frequency of which is stated as 100 by Young.

This line was also seen very brilliantly in the tube supplied to me by Professor Ramsay on May 1, and on May 6 it was compared directly with the chromosphere line by Mr. Fowler. The second order grating spectrum was employed. The observations in this region were not so easy as in the case of D₃, but with the dispersion employed, the gas line was found to be coincident with the chromospheric one. In this case also, the chromosphere was observed at the sun's poles, in order to eliminate the effects due to the sun's rotation.

In a former note (*Roy. Soc. Proc.*, vol. lviii., p. 114), I have pointed out that this line does not appear in the spectra of the gases obtained from all minerals which give the yellow line.

Besides appearing in the spectrum of the chromosphere, the line in question is one of the first importance in the spectra of nebulae, bright line stars, and of the white stars such as Bellatrix and Rigel.

The Infra-red Line, λ 7065.5.—In addition to D₃, and the line at 4471.8, there is a chromospheric line in the infra-red which also has a frequency of 100, according to Young. On May 28, I communicated a note to the Royal Society stating that this line had been observed in the spectrum of the gases obtained from bröggerite and euxenite (*Roy. Soc. Proc.*, vol. lviii.), solar comparisons having convinced me that the wave-length of the gas line corresponded with that given by Young; and I added "it follows, therefore, that besides the hydrogen lines, all three chromospheric lines in Young's list which have a frequency of 100 have now been recorded in the spectra of the new gas or gases obtained from minerals by the distillation method."

M. Deslandres, of the Paris Observatory, has also observed the line at 7065 in the gas obtained from clèveite (*Comptes Rendus*, June 17, 1895, p. 1331).

Other Lines.—Determinations of the wave-lengths of many other lines in the spectra of the new gases have been made, chiefly with the aid of a Steinheil spectro-scope having four prisms, and the results leave little doubt as to the coincidence of several lines with those appearing in the chromosphere, nebulae, and white stars.

It seems very probable, also, that many lines which have been noted, and for which no origins have yet been traced, belong to gases which have not hitherto been recorded in the chromosphere.

The accompanying table summarises the chief lines which have so far been recorded in the new gases from various minerals, some of which show D₃ while others do not. Only those lines which also appear in the spectrum of the chromosphere, nebulae, or Orion stars, are given in the first instance. There are other lines which are probably also associated with chromospheric ones, but further investigation of them is considered desirable before they are included in the list.

The first column of the table gives the wave-lengths of the lines on Rowland's scale, while the second gives the wave-lengths on Angström's scale; the third gives the frequency of the lines in the chromosphere according to Young. In the fourth column lines photographed with the prismatic camera during the total eclipse of April 16, 1893, are shown; these have been included because in some cases lines which appear to be comparatively unimportant in Young's list were photographed as important lines. The fifth column indicates probable coincidences with lines in the spectrum of the Orion nebula; the accuracy of these wave-lengths is of necessity less than in the case of the chromosphere; with the exception of D₃ they are taken from my paper on the photographic spectrum of the Orion nebula (*Phil. Trans.*, 1895, vol. clxxxvi. A, p. 76). The sixth column shows probable coincidences with dark lines in the spectrum of Bellatrix, this being taken as an example of the Orion stars (*Phil. Trans.*, 1893, vol. clxxxiv. A, p. 695), the lines 4922.3 and 5015.8 have been photographed since the date of the paper to which reference is made.

The last column gives the wave lengths, from Mr. Crookes's table, of the lines observed by both of us.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on December 2nd, Sir James Crichton-Browne presiding. The following were elected Members:—Messrs. C. H. Berners, J.P., J. M. Bruce, M.D., F. Chambers, A. M. Chance, J.P., A. E. Fletcher, F. Fox, J.P., H. Seymour, K. T. Stewart, M.D., G. H. Strutt, F. Tendron, F.G.S., W. H. Warner, M. Webb, J.P., and Mrs. S. H. Phillips.

EXPERIMENTAL PROOF OF VAN 'T HOFF'S
CONSTANT, OF ARRHENIUS'S GENERALISA-
TION, OF OSTWALD'S LAW OF DILUTION,
OF DALTON'S LAW, &c.,
IN VERY DILUTE SOLUTIONS.*

By Dr. MEYER WILDERMANN.

THE following forms the foundation of the new theory of solutions:—

1.—Proof of van 't Hoff's Constant.

It was van 't Hoff who first drew attention to the fact that the equations representing the generalisations arrived at by Boyle, Gay-Lussac, and Avogadro in the case of gases are equally applicable to dissolved substances, if the osmotic pressure of the molecules of the dissolved substance be substituted for the pressure of the gas. Van 't Hoff deduced these laws for solutions from thermodynamical considerations (*Zeit. Phys. Chem.*, i., 1887)—a method which gives them increased validity—and illustrated them from the osmotic experiments of Pfeffer and de Vries. Soon after, Prof. Max Planck deduced van 't Hoff's laws in a very elegant way, also from thermodynamical considerations (*Wied. Ann.*, xxxii., 1887). Lorentz (*Zeit. Phys. Chem.*, vii.), Boltzmann (*Zeit. Phys. Chem.*, vi., vii.), Riecke (*Zeit. Phys. Chem.*, vi.), and Van der Vaals (*Zeit. Phys. Chem.*, v.) have deduced the gaseous laws from the kinetic theory.

At the same time van 't Hoff was able to establish a thermodynamical relation between the osmotic pressure of a dissolved substance and the molecular lowering of freezing-point of the solution, thereby furnishing a rational basis for the empirical generalisations of Raoult, Babo, and Wüllner, who had previously investigated the same point (*Zeit. Phys. Chem.*, i.); later on Planck deduced the same thermodynamical relations (*Wied. Ann.*, xxxii., 1887).

In van 't Hoff's thermodynamical argument the solutions are assumed to be very dilute, and hence their experimental verification is of special importance in very dilute solutions. The determination of the molecular freezing-point is the safest and the most convenient method of testing the validity of these generalisations experimentally, and this has been done for moderately dilute solutions by van 't Hoff himself, and by Eykmann, and the equation—

$$t = \frac{0.02 T^2}{w};$$

where T = absolute temperature, w = latent heat of fusion of the solvent, has been experimentally verified and confirmed for several solvents. The method of determining the freezing-point in very dilute solutions of my late friend P. B. Lewis (*Trans. Chem. Soc.*, 1894; a fuller account has been given in *Zeit. Phys. Chem.*, xv., p. 358), my investigations on the same matter ("On the Determination of the Freezing-point of Water," *Zeit. Phys. Chem.*, xv., p. 365. See "On the Real and Apparent Freezing-points and the Freezing-point Methods," then "On the Determination of Freezing-point in Dilute Solutions to 0.4° Depression," which I shall publish shortly in *Phil. Mag.* and in *Zeit. Phys. Chem.*) give us the possibility of submitting van 't Hoff's equation,—

$$t = \frac{0.02 T^2}{w},$$

to a more accurate verification. I give a full account of the freezing-point method, since it is important to know not only what one gets, but how it is got. This is especially necessary in view of the different contradictory results which have been published and are due to insuffi-

cient, and often more than insufficient, development of the method used. Last year I investigated a series of bodies (*Phil. Mag.*, July, 1895); this year I investigated cane-sugar, urea, alcohol, dextrose, resorcin, maltose, milk-sugar, glycerin, with the convergence temperature above and below the freezing temperature, with the r_{10}° and the r_{10}° thermometer, with different parts of the scale. The obtained results are in excellent agreement with van 't Hoff's theory.

2.—Arrhenius's Generalisation.

Van 't Hoff showed, by four different methods, that a generalisation analogous to that of Avogadro was valid for solutions of non-electrolytes, like cane-sugar; it then became of importance to account for exceptional cases, in which the depression of the freezing-point was abnormal, and in particular the cases of salts, acids, and bases in aqueous solutions. The explanation was given when Arrhenius showed that, by two independent, quite different, methods, the observation of the lowering of freezing-point and of the electrical conductivity of a solution, the same value would be obtained for the factor i , which denotes the ratio of the pressure actually exerted by the substance to the pressure which the substance would exert if it consisted entirely of undissociated molecules. Arrhenius made determinations on about forty bodies in moderately dilute solutions of various concentrations, and verified his generalisation. From the intimate connection which exists between van 't Hoff's laws and the dissociation theory, it follows also that the generalisation of Arrhenius may find a more exact experimental confirmation in dilute solutions. This is not only important on account of the great light which the theory of dissociation has thrown upon the two provinces of chemistry and physics, but it is also important inasmuch as thereby the laws of van 't Hoff will find in every point their more exact confirmation (see also Max Planck, *Wied. Ann.*, xxxiv.).

Last year I investigated sulphuric acid, potassium chloride, dichloroacetic acid, orthonitrobenzoic acid, trichloroacetic acid, with the convergence temperature above the freezing temperature (*Phil. Mag.*, July, 1895); this year, with the convergence temperature below the freezing temperature. Besides these bodies I investigated nitric acid, hydrochloric acid, potassium chloride, sodium chloride, ammonium chloride, &c., with the convergence temperature below the freezing temperature. Arrhenius's generalisation finds the most wonderful confirmation.

3.—The Law of Dilution.

This forms one of the most important foundations of the theory of dissociation. It was Ostwald who first showed the relation between the dissociated and undissociated molecules to depend upon the action of masses, and took pains to verify the same in the case of about two hundred acids by means of their electric conductivity (see, also, Max Planck, *Wied. Ann.*, xxxiv.).

From the above-mentioned generalisation of Arrhenius it follows that the law of dilution ought also to be deducible from the freezing-points, since the freezing-points, as well as the electric conductivity, enable us to know the degree of dissociation, and it may be interesting inasmuch as we have not here to do with velocity of ions or with the theory of electric conductivity.

From the intimate connection which exists between van 't Hoff's laws and the theory of dissociation, it follows that the law of dilution must find its experimental confirmation in dilute solutions; the freezing-point methods have not been till now sufficiently exact for this purpose; now we are able to undertake it under favourable conditions.

I investigated orthonitrobenzoic acid, dichloroacetic acid, trichloroacetic acid, with the convergence temperature above (*Phil. Mag.*, July, 1895) and below the freezing temperature, and found that the law of dilution finds a good confirmation also by this second way.

* Read before the British Association (Section B), Ipswich Meeting, 1895.

4.—*Dalton's Law in Solutions.*

Dalton's law, as we know, declares that the total pressure of a mixture is equal to the sum of the partial pressures exerted by the constituents of the mixture in the given space. This law, for the same reason as the law of Boyle and Gay-Lussac, holds good only in the case of dilute gases. Since van't Hoff has shown that the law of Boyle and Gay-Lussac is to be applied for dilute solutions (see van't Hoff's constant), the conclusion may logically be drawn that the third gaseous law—the law of Dalton—exists in solutions also. For some reasons, which cannot be further discussed here, the best mode of testing Dalton's law in solutions is the freezing-point method. I investigated, for this purpose, mixtures of urea and resorcin, of urea and cane-sugar, of urea and dextrose, of dextrose and cane-sugar; the obtained results, in very dilute solutions (with the convergence temperature under the freezing-point), are very satisfactory—no less than in the case of the proof of van't Hoff's constant.

5.—*On the Degree of Dissociation in Solutions when Non-electrolytes are present.*

It has been found that the degree of dissociation of a gas does not change in the presence of an indifferent gas. This is also to be regarded as a consequence of Dalton's Law for the partial pressures of the constituents of a mixture. I find the relations to be quite analogous in the case of electrolytic dissociation. I investigated the influence of glycerin upon dichloroacetic acid, upon orthonitrobenzoic acid, &c.; the result is, that no change (at any rate no considerable change) in the degree of dissociation takes place, even in the case of dichloroacetic acid and orthonitrobenzoic acid. These investigations of the influence of non-electrolytes on the degree of dissociation by the method of freezing-points is of special interest, since, besides the phenomena under consideration, the theory of electric conductivity can be more easily surveyed and understood by this than by using the method of electric conductivity (as has been done by Arrhenius) where the above phenomenon is complicated by the change of the velocity of ions, owing to the change of the inherent viscosity ("innere Reibung") of the liquid. Using the method of freezing-points, we are able to isolate the phenomena and to come to a clear conception of both of them. At any rate no considerable reduction of the degree of dissociation, I find, takes place when non-electrolytes are present, and the diminution of the electric conductivity of a dissolved electrolyte in the presence of a non-electrolyte must, more or less, be entirely attributed to the change of the inherent viscosity.

6.—*On the Reduction of the Degree of Dissociation by introducing a Common Ion.*

I have already drawn attention to the importance of the law of dilution as a proof of the theory of dissociation, which shows that the relation between the dissociated and undissociated molecules depends upon the well-investigated and established law of action of masses. A second proof of the theory of dissociation, based upon the same law of action of masses, is the reduction of the degree of dissociation by the introduction of a common ion. In the case of a dissociated gas, a reduction of the degree of dissociation takes place if one of the dissociated parts is introduced. It was Arrhenius who first, in his paper, "Theory of Isohydic Solutions" (*Zeits. Phys. Chem.*, ii.), drew attention to this important point, as a proof of the theory of dissociation. Arrhenius himself proved this question but little, using the method of electric conductivity. A more searching investigation of this matter by the method of electric conductivity has been undertaken at the same time by Prof. Ostwald in Leipzig, and myself in Oxford. It is important to mention that the agreement between the theory and the obtained results is very satisfactory. Here I give the results which I obtained

by the investigation of the same matter in dilute solutions by a second method—the freezing-point method. I investigated the reduction of dissociation in the case of mixtures of hydrogen chloride and orthonitrobenzoic acid, hydrogen chloride and dichloroacetic acid, nitric acid and orthonitrobenzoic acid, nitric acid and dichloroacetic acid, nitric and hydrochloric acid, &c. I have calculated, owing to want of time, only a part of my experimental results, and, as far as my calculations have been carried out, the agreement between the theory and the experiments is quite satisfactory. I draw attention to the fact that, while non-electrolytes did not produce reduction of dissociation in the case of dichloroacetic acid and orthonitrobenzoic acid, we, quite in accordance with the law of action of masses, have been able for the same bodies, by introducing common ions, to observe reductions of dissociation which amount even to 60 or 70 per cent of the total value of the degree of dissociation.

Christ Church, Oxford.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 261.)

B. *Air of the Laboratory.*—The laboratory, situated on the second floor, consisted of two rooms, one of which looked on to the street and the other on to the garden. These rooms communicated with each other by a door, and had in addition a door opening on to the landing, which supplied them with air coming from the roof or basement, according as the door of the loft or basement was open or shut.

The apparatus for condensing vapour from the air was freely suspended in the back room, in a very large glass cage, having in its upper part a large opening which could be lessened at will, connected with a ventilating shaft, and receiving air from the room through a large opening 70 c.m. above the floor.

The spectroscope was placed in the same room, 1.5 metres from the condensing apparatus. The front room, the landing-door of which was open, supplied air to the back room.

1st. The wind was blowing from the east, the air came from the yard in the south-west, by the staircase well and the landing. The temperature of the air in the glass cage was 22.5°; dew-point was 15.2°. The weight of water condensed was 132 grms. During the period of condensation of water vapour, the temperature of the disulphide of carbon was between 0° and 3°. The flame of a gas-lamp burning close to the apparatus was blue slightly tinged with violet, and spectrum analysis of this flame showed a persistent weak sodium line masking any other spectrum.

I only succeeded in realising these conditions by the care I took in dusting both rooms, and everything in them, two days previously, in having the floors carefully washed as well as the stairs, and in abstaining from working in the laboratory. When I did not take these precautions I always saw bright points in the flame.

Five drops of a 10 per cent solution of nitrate of silver caused a slight precipitate in 10 c.c. of filtered water. One drop of a saturated solution of chloride of barium, added to 15 c.c. of filtered water, gave no precipitate; but the mixture, when evaporated down to about half a c.c., became perceptibly clouded.

One hundred c.c. of filtered water left, on evaporation, a rich yellow stain weighing 0.000065 gm. The stain turned black when heated; the residue was dissolved by two drops of water, and the solution when put into the flame coloured it yellow, intensely but temporarily. Spectrum analysis showed the sodium line and a very faint calcium spectrum.

The inner filter, through which the water passed, when dried, was the same colour as paper exposed to the atmospheric dust of the laboratory. Under the microscope I saw a number of black and sparkling grey specks, as well as filaments. After burning the carbon made by carbonising the inner filter in a closed vessel, there remained a brown ash weighing 0.000105 gm. During combustion, the part of the flame affected was coloured deep yellow. The ash, when moistened with chloride of ammonium and put into the flame, showed sodium and calcium spectra, but not a trace of a potassium spectrum. The residue, when treated thrice with fluoride of ammonium to eliminate the silica, and put into the flame, still showed the sodium line without the potassium line. Lastly, the brown marks left on the fine platinum wire loop, when treated with pure sulphuric acid and put once more into the outer envelope of the flame, showed the sodium line still, with a very faint calcium spectrum, but no trace of the potassium line.

2nd. *Air from the street*, running east and west, entering by an opening on the south, by way of the roof and loft:—

The air brought into the laboratory by the draught of four ventilating shafts with which it was furnished, coloured a Bunsen flame distinctly violet; on spectrum analysis, a faint but decidedly yellow sodium line was seen, without a trace of the calcium spectrum; outside, the air temperature was 27.3°; in the glass case it was 23.8°, and dew-point was 17.7°; there were collected 135 grms. of filtered water, neutral to litmus-paper.

Five drops of a 10 per cent solution of nitrate of silver made a sensible precipitate in 20 c.c. of filtered water.

Twenty c.c. of filtered water were evaporated down to about half a c.c. This liquid was sensibly clouded by adding one drop of a saturated solution of chloride of barium.

One hundred c.c. of filtered water, when evaporated to dryness, left a sparkling brown stain, weighing 0.000057 gm. This residue blackened when heated; when dissolved in two drops of water, and put into a flame, the solution coloured it yellow. Spectrum analysis showed the sodium line, as well as a faint calcium spectrum.

The inner filter, through which the water passed, when dried, was the same colour as paper exposed to the dust of the laboratory; under the microscope it showed sparkling and transparent black and grey specks, stains just like clay, moistened and dried, as well as organic filaments, some long, others short.

After burning the carbon made by carbonising the filter in a closed vessel, there remained a brown siliceous ash, weighing 0.000147 gm. During combustion, spectrum analysis showed a strong sodium line. This ash, when moistened with chloride of ammonium, coloured the flame intense yellow, showed a sodium spectrum and a faint calcium spectrum all the time, but no traces of a potassium spectrum.

Having eliminated the free and combined silicic acid by means of fluoride of ammonium, then treating the residue with sulphuric acid, I detected in the product faint indications of the presence of sodium, calcium, aluminium, and iron; but I utterly failed to find any trace of potassium.

If we admit that the methods I adopted for ascertaining the nature and amount of sodium and calcium compounds in the air give correct results, we must conclude from them that air, when deprived by rain of the dust it had in suspension, and kept saturated or nearly so by rain, does not contain in from 10 to 15 cubic metres an amount of soluble sodium compounds capable of being weighed in a balance weighing to three thousandths of a mgm. There is sodium in it nevertheless, although spectrum analysis of a Bunsen flame burning in it does not show the sodium line.

In this manner the presence of sodium is accounted for in hygroscopic bodies, other than sodium compounds, exposed to the air and sheltered from dust particles; for

they—by liquefying it by absorption of, and depositing it by condensation of, the water in the air—persistently give indications of the presence of the metal sodium. Such are undoubtedly the chlorides of calcium and lithium, as I show in chapters devoted to the chemical and spectroscopic studies of these bodies. Neither outside nor inside air, when still, contains a measurable amount of soluble sodium compounds in from 10 to 15 cubic metres, although they give the sodic characteristics to flames. The quantity of insoluble sodium and calcium mineral matters in this amount of air varies from six to fifteen hundredths of a mgm.

I have noted the presence of potassium amongst the mineral matters in free air in certain districts.

In spite of all efforts I cannot detect a trace of either soluble or insoluble potassium compounds in the air of the higher part of Brussels.

Rain Water.—I thought it useful to check my researches in air by making a comparative examination of the water condensed from saturated air, and rain water collected when there was no wind. I worked with rain which fell by day as well as by night, in order to better understand the part played by chimneys in contaminating the air.

The rain water was collected in the middle of the garden, 1 metre above the ground, after the air had been washed by several days' drizzle. Under these conditions it seemed that the rain water ought only to contain traces of the mineral matters in the clouds supplying the rain, to which would be added the compounds emanating from chimneys.

To collect the rain water, I put on a board, 1 metre above the lawn, five Bayeux porcelain dishes, 40 cm. diameter. In addition I arranged, at a side of the yard leading to the garden, a cloth to shelter the spectroscopic, Bunsen lamps, and everything I wanted to filter and evaporate the collected rain water. All experiments on rain water were conducted in the open air, which was saturated with moisture but not misty. As it was collected the water was poured into a covered platinum vessel, and filtered after weighing. I used for this purpose double filter-papers, which were first treated with dilute and pure nitric and hydrofluoric acids, and finally with water. The double filter-papers were arranged in a platinum funnel passing through a hole in a sheet of polished glass on a platinum retort, in which was collected the weighed and filtered water.

To ascertain the nature and quantity of matters either dissolved or left in the filter, I did as I have described above with water condensed from the vapour in the air.

Whilst I was collecting the rain water I worked the condensing apparatus outside the window on the second floor and sheltered from the rain, so as to be able to compare both results.

Rain Water fallen during the Day.—Wind, none; temperature of the air, 8.13°; rain water collected between 8 a.m. and 3 p.m., 153 grms.

All day long the Bunsen lamp burnt in the yard, under the canvas, which was quite soaked with the rain, without showing a trace of the sodium line on spectrum analysis. It was the same outside the second floor window under cover, where the apparatus for condensing the atmospheric moisture was working. Dew-point was 7.90°. The water collected weighed 138 grms.

The filtered rain water was colourless, and neutral to litmus-paper. When sprayed into a Bunsen flame, burning in the court under the wet canvas, by means of a metallic injector with steam from pure water, it turned the flame distinctly yellow. Spectrum analysis of the yellow flame showed the sodium line, hitherto invisible in the flame burning in air, or in the flame with pure water coming from the spray, which had been purified from sodium dust.

Five drops of a 10 per cent solution of nitrate of silver made a very decided precipitate in 20 c.c. of filtered rain water. Five drops of a 10 per cent solution of nitrate of

silver made a very slight cloudiness in 20 c.c. of filtered water of condensation. One drop of a saturated solution of chloride of barium gave no precipitate in 10 c.c. of filtered rain water. After evaporating 20 c.c. of rain water down to about half a c.c., the residue was very slightly clouded by one drop of a saturated solution of chloride of barium; whereas after evaporating 18 c.c. of water of condensation down to about half a c.c., the residue was not affected in the slightest degree by one drop of a saturated solution of chloride of barium.

Filtered rain water, when being evaporated on a bath, emitted a smell of fog similar to that noticed after rain. One hundred c.c. of this water, when evaporated down to about 1 c.c., yielded a cloudy brownish yellow liquid. This liquid, when evaporated to dryness on the bath, left a brown hygroscopic residue weighing 0.000191 grm., whilst 100 c.c. of water of condensation left a brown stain weighing only 0.000027 grm. The residue left, after evaporating the rain water to dryness, turned very black, and emitted a smell like coal-tar, when raised to a dull red heat in a closed vessel. This residue, when dissolved by a few drops of water and put into a Bunsen flame, coloured it yellow, and showed on spectrum analysis a brilliant but temporary sodium spectrum, as well as a weak and incomplete calcium spectrum, but no trace of the potassium line.

The filter through which the rain water had passed, when dried, showed a dark grey tint all over its surface, a vast number of black specks, and also filaments. When carbonised in a closed vessel, and then burnt, it left a reddish brown siliceous ash, weighing 0.000225 grm. per 100 c.c. of filtered water.

During combustion I saw the sodium line, but no trace of a calcium or potassium spectrum. When moistened with chloride of ammonium, the ash showed an ill-defined sodium and a very weak calcium spectrum. After eliminating the free and combined silicic acid by means of fluoride of ammonium, and then treating it with sulphuric acid, I still saw a sodium and a very weak calcium spectrum, but no potassium line.

The inner filter, through which the water of condensation from atmospheric vapour had passed, when dried, carbonised, and burnt, left 0.000042 grm. of brown siliceous ash, containing sodium and slight traces of calcium; but I could not detect the presence of potassium in it by spectrum analysis.

Rain Water fallen during the Night.—There had been a fine rain all night, but no wind. The results of the experiments were of the same nature as those above. For instance, it was necessary to concentrate the filtered water to $\frac{1}{10}$ th of its volume in order to detect, with nitrate of silver, the presence of chlorine, and to $\frac{1}{10}$ th of its volume to prove the presence of sulphuric acid by means of chloride of barium.

The residue, after evaporating 100 c.c. of filtered water, was brown and weighed 0.000115 grm., and consisted chiefly of tarry matters, with traces of volatile compounds of sodium and calcium, but not of potassium.

The filter through which the nocturnal rainfall had passed was considerably less stained than that used to filter rain fallen during the day, and the weight of the brown ash left on burning it was only 0.000098 grm. per 100 c.c. of filtered water,—that is to say, less than half the weight of the ash of the filter through which an equal volume of rain water collected by day had passed, which was 0.000225 grm.

This last fact tends to show that, when there is no wind, the chimneys contribute largely to the contamination of the air by the mineral matters which are found in it near crowded neighbourhoods, and that the remainder may perhaps be attributed to rain clouds. But before coming to a general conclusion these experiments ought to be tried a great number of times, and this can hardly be done excepting in a building fitted up for meteorological research.

I ascertained, besides, by many trials, that the rain

entrapped the soluble and insoluble matters suspended in the air so thoroughly, that, after very heavy rain, the last showers gave water so free from chlorides and sulphates that I had to evaporate it down to $\frac{1}{10}$ th of its original volume before I could detect chlorine and sulphuric acid in it by nitrate of silver and chloride of barium. During the summer of 1881 I not only found that chlorine and sulphuric acid were not present in the rain which fell at the end of a very heavy storm, but after the rain ceased I found the outer air left for several hours during the day in such a state of purity that it was absolutely impossible to detect a trace of the sodium line in the spectrum of a Bunsen flame burning in it.

With very rare exceptions coal and coke are used in Brussels as fuel; I attribute to this the absence of potassium, for it has been detected in the atmospheric dust of other districts.

I think it is scarcely necessary to mention that the results given above are only applicable to the atmospheric conditions existing at the time of my experiments. In truth, long experience has taught me the great variation in the nature of atmospheric dust, according to the prevailing winds. I cannot say that I have on a single occasion found the air of the higher part of the town the same twice running as regards dust. The air appears most free from mineral dust after a fine rain without wind, and whilst it continues raining. In this case the suspended dust particles are always blackened by coal-smoke.

I have ascertained beyond a doubt, by observations extending over more than a third of a century, that the dust brought by the air, with or without rain, shows a density of colour, always varying according to the direction of the wind which brings it.

The air which passes over the town from the north or north-west, towards the south or south-west before reaching the street in which I live, always brings with it a fine siliceous dust more deeply blackened by coal-smoke than that entrapped by the fine rain which falls when there is no wind. The air brought by a south or south-east wind, with or without rain, brings a greasy, more or less yellow, dust.

Lastly, the air brought by an east wind, with or without rain, brings a grey dust, with a sandy, clayey character.

According as buildings are raised in my neighbourhood, which was originally quite open, on the east, south, or south-west, so have the physical properties of dust deposits remarkably changed, without, however, attaining each other's specific characteristics.

The facts I have mentioned here ought to be met with in all districts. Whenever accurate observations are made everywhere, no doubt we shall find that they are due to the dust of the air as well as to the water which flows along the ground, abstracting from it the soluble bodies it contains, no matter what may be the nature or origin of these bodies.

The nature of the dust particles ought to have some connection with the composition of the soil swept by the wind, and the smoke poured into the air by factories and chimneys.

(To be continued).

King's College.—Free Lecture.—On Monday next, the 9th inst., a Free Lecture will be given to the Public, in the Theatre of the College, by Prof. Thomson, F.C.S., &c., on "Movements of Gases and Liquids" (Experimentally Treated), commencing at 8 p.m.

On the Neutral Crystalline Calcium Chromite.—E. Dufau.—At a sufficiently high temperature chromium sesquioxide combines directly with lime, forming a chromite of the formula $\text{Cr}_2\text{O}_3\text{CaO}$. It is crystalline and stable at the highest temperatures. Its specific gravity is 4.8 at 18°, and it resists the action of the most powerful acids.—*Comptes Rendus*, cxxi., No. 20.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 7th, 1895.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

(Concluded from p. 266).

125. "Normal Hexane from Light Petroleum (Petroleum Ether)." By G. L. THOMAS, B.Sc., and SYDNEY YOUNG, D.Sc., F.R.S.

Having devised an improved form of dephlegmator (CHEMICAL NEWS, lxxi., 177) we determined to attempt the separation of a pure paraffin from "petroleum ether" in the same way that ethyl acetate was separated from a mixture of methyl, ethyl, and propyl acetates (*Phil. Mag.*, 1894, 8).

Each fraction was weighed, and its temperature range noted and corrected for the thermometric error and for the difference between the barometric reading and 760 m.m. The ratio of the weight of any fraction (Δw) to its temperature range (Δt) gives, as a rule, a measure of the purity of the liquid, though in the early fractionations of a complex mixture this cannot be relied on.

Thus, in the 4th fractionation the fraction coming over between 65° and 66° had the highest value of $\Delta w/\Delta t$, whereas in the 16th fractionation the corresponding fraction (65° to 66° 85') had the lowest value. At an early stage of the work it appeared, therefore, as though a single substance boiling at about 65° or 66° was being separated from liquids boiling at much higher and lower temperatures (above 90° and below 40°); but the later fractionations showed that instead of a single substance boiling at about 65° or 66°, there were really two liquids—one boiling at 69°, and the other at about 61° (normal and iso-hexane).

As the number of fractions was very large, it was decided after the 16th fractionation to proceed only with the separation of normal hexane, and after 31 preliminary fractionations it was considered that the separation had proceeded far enough for the final series of fractionations to be undertaken, as in the case of ethyl acetate (*loc. cit.*). The hexane obtained by the final fractionation of the fractions boiling at and above 69° 05', when distilled from phosphorus pentoxide, boiled at 69° 1', or only 0° 1' higher than the hexane prepared from propyl iodide, but its sp. gr. at 0° (0.68478) was 1.15 per cent higher. The hexane was then treated with a mixture of concentrated sulphuric and nitric acids, when considerable heat was evolved, and the acid became yellow, and was found to contain some m-dinitrobenzene in solution. The impurity present was therefore benzene or possibly hexanaphthene, or both.

The remaining high-boiling fractions were treated with the mixed acids and were refractionated; the low-boiling fractions also were treated in the same manner before their final fractionation, and in every case it was found that m-dinitrobenzene was formed.

By further long-continued treatment of the two specimens of hexane with the mixed acids and subsequent distillation, a quantity was finally obtained boiling at 69° 05' and with the sp. gr. 0.67813 at 0°, or only 0.17 per cent higher than that of pure hexane.

The vapour pressures and specific volumes—as liquid and as saturated vapour—were determined at a few temperatures, and the critical temperature and pressure were also observed; the results differed but slightly from those obtained with the hexane from propyl iodide. The critical constants of both specimens are given below:—

	Critical temperature.	Critical pressure.
Hexane from petroleum ether ..	235.15	22560
Hexane from propyl iodide ..	234.8	22510

The hexane was evidently very nearly pure, but the

separation of this paraffin from petroleum ether is only possible by long-continued fractional distillation with an efficient dephlegmator, and by removal of benzene or hexanaphthene with nitric and sulphuric acids.

126. "The Vapour Pressures, Specific Volumes, and Critical Constants of Normal Hexane." By G. L. THOMAS, B.Sc., and SYDNEY YOUNG, D.Sc., F.R.S.

The normal hexane employed was obtained from Kahlbaum, and prepared by the action of sodium on propyl iodide. It was purified by treatment with concentrated nitric and sulphuric acids and subsequent fractional distillation.

The boiling-point at 760 m.m. is 69° 0', and the sp. gr. at 0° is 0.67696. The critical constants are—

Critical temperature ..	234.8°
Critical pressure ..	22510 m.m.
Critical volume of a grm...	4.268 c.c.

The vapour pressures and the volumes of a grm.—as liquid and as saturated vapour—were determined, and a limited number of observations of pressure and volume of unsaturated vapour were made at a series of temperatures with the object of finding whether the isochors showed any indication of curvature. As in the case of isopentane (in about the same volume region) the isochors were found to be very slightly curved, the values of dp/dt diminishing with rise of temperature. The deviations from constancy become smaller as the volume increases.

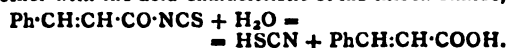
The absolute temperatures and molecular volumes of liquid and saturated vapour were read from the curves at a series of pressures "corresponding" to those given in previous papers, and the ratios of the absolute temperatures and of the volumes to the critical constants were calculated. These ratios agree with those of isopentane and benzene; normal hexane therefore belongs to Group I. in the classification of substances previously adopted (*Trans. Chem. Soc.*, lxiii., 1257; *Phil. Mag.*, 1894, 1), and the molecules of the liquid are probably simple like those of the gas.

The absolute temperature ratios at corresponding pressures are higher for hexane than for isopentane; in this respect the paraffins seem to resemble the esters (*Trans. Chem. Soc.*, lxiii., 1252), for which the ratios increase without exception with rise of molecular weight. In the case of the esters, the volume ratios appear to be independent of molecular weight, but—for isomeric compounds—to depend to some extent on the constitution. It seems probable that this may also be the case for the two paraffins studied, but an investigation of other paraffins will be necessary before these points can be decided.

The ratio of the actual to the theoretical density at the critical point is 3.83, the mean value for the other members of Group I., including carbon dioxide (Amagat) and isopentane, being 3.75.

127. "Acidylthiocarbimides." By AUGUSTUS E. DIXON, M.D.

This paper gives an account of further experiments (see Dixon and Doran, *Trans. Chem. Soc.*, 1895, lxxvii., 565) on the production of thiocarbimides containing acidic radicles. By heating the chloride of valerianic or of cinnamic acid with lead thiocyanate in presence of anhydrous benzene, valeryl or cinnamoyl thiocarbimide is formed, and passes into solution. Both these thiocarbimides have a slightly pungent odour, and attack the eyes, causing a flow of tears, the former being especially active. They are readily desulphurised by lead or silver salts, but decompose in presence of water, yielding thiocyanic acid, together with the acid characteristic of the thiocarbimide,—



By bringing the solutions into contact with ammonia, amines, or ethyl alcohol, the corresponding thioureas, thiocarbimides, or thiourethanes, respectively, are produced.

The following compounds are described:—

ab-Valerylphenylthiocarbamide, $\text{BuCO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$; sym. valerylphenylurea, $\text{BuCO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$; ab-valerylorthotolylthiocarbamide, $\text{BuCO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{o-To}$; sym. valerylorthotolylurea; ab-valerylparatolylthiocarbamide, $\text{BuCO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{p-To}$; valeryl- α -naphthylthiocarbamide, $\text{BuCO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\alpha\text{-Napt}$; n-valeryl- ν -benzylphenylthiourea, $\text{PhCH}_2\cdot\text{N}(\text{Ph})\cdot\text{C}(\text{SH})\cdot\text{N}\cdot\text{COBu}$; valerylthiourea, $\text{CSN}_2\text{H}_3\cdot\text{COBu}$; valeryl- β -thiourethane, $\text{BuCO}\cdot\text{NH}\cdot\text{CS}\cdot\text{OC}_2\text{H}_5$; ab-cinnamoylphenylthiocarbamide, $\text{PhCH}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$; ab-cinnamoylorthotolylthiocarbamide, $\text{PhCH}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{o-To}$; ab-cinnamoylparatolylthiocarbamide,—

$\text{PhCH}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{p-To}$;

ab-cinnamoylphalanaphthylthiocarbamide,—

$\text{PhCH}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\alpha\text{-Napt}$;

cinnamoylthiourea.—

$\text{CSN}_2\text{H}_3\cdot\text{COCH}\cdot\text{CHPh}$; $\text{PhCH}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{OC}_2\text{H}_5$, cinnamoyl β -thiourethane. All the thioureas above named, with the exception of the valeryl benzoylphenyl compound, are desulphurised by heating with alkaline lead tarrate.

It is proposed to extend these experiments with lead thiocyanate, in the hope of obtaining thiocarbamides derived from other acids than those only containing the group $\text{CO}\cdot\text{Cl}$; for example, picric, phenylsulphonic, and ethyl sulphuric acids.

128. "Some Constituents of the Root of '*Polygonum cuspidatum*.'" By A. G. PERKIN.

Polygonum cuspidatum is a native of China and Japan, and flourishes in parts of India and Russia. The freshly gathered roots consist of a thick, succulent bark, of an orange-red colour, and a central woody portion of a light yellow tint.

The principal constituent of the root bark was found to be a glucoside, $\text{C}_{22}\text{H}_{20}\text{O}_{10}$, crystallising in lustrous yellow needles melting at $202\text{--}203^\circ$. On hydrolysis, this yielded 61.82 per cent of a product which was recognised as emodin, the reaction—



requiring 62.5 per cent of emodin. This glucoside, for which the name *cuspidatin* is proposed, differs considerably in properties from frangulin, $\text{C}_{21}\text{H}_{20}\text{O}_9$, the glucoside of emodin which is contained in the bark of the *Rhamnus frangula*.

A second glucoside was also isolated, but in too small quantity for analysis. On hydrolysis it yielded a crystalline substance melting at 199° , which by treatment with sulphuric acid at 160° was converted into emodin. It was found to be identical with the emodin monomethyl ether previously isolated from the root bark of *Ventilago madraspatama* (*Trans. Chem. Soc.*, 1894, 923). The other substances found were a small amount of free emodin and a wax which crystallised in colourless leaflets melting at $134\text{--}135^\circ$. This latter was found to be identical with the wax $\text{C}_{18}\text{H}_{28}\text{O}$, present in the root bark of the *Morinda umbellata* (*Trans. Chem. Soc.*, 1894, 854).

An examination is being carried out of the constituents of the roots of the *Polygonum bistorta* and *Rumex nepalensis*, which are closely allied to this plant.

129. "Notes on the Action of Hydrofluoric Acid upon Crystallised Silicon." By G. S. NEWTH.

It is generally stated that hydrofluoric acid is without action upon crystallised silicon; that while amorphous silicon is attacked by it, this acid is incapable of acting upon the crystallised element.

This statement, however, requires to be made with some reservation, for although it is doubtless true of the aqueous acid, and possibly of the liquid acid, it is not true of the gas.

If acid potassium fluoride be heated in a platinum retort, and the pure gaseous hydrofluoric acid so produced be allowed whilst hot to blow upon a little heap of crys-

tallised silicon supported on a porcelain crucible lid, the silicon at once takes fire and burns brilliantly in the gas, forming silicon fluoride and hydrogen.

If the neck of the retort be more than an inch or two in length, it is necessary to heat it in order to keep the gas sufficiently hot, but if it be quite short, the temperature of the gas as it is disengaged from its compound is sufficiently high to enable it to attack the silicon.

The importance of this observation lies in the fact that the spontaneous ignition of crystallised silicon is generally regarded as in all cases a sufficient test for free fluorine; but it is evident that unless the temperature of the gas is below a certain point the combustion of silicon is not a safe criterion.

130. "Note on the Periodides of Theobromine." By G. E. SHAW.

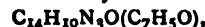
Apparently only one periodide of theobromine has been previously described, viz., that having the formula $\text{C}_7\text{H}_8\text{N}_4\text{O}_2\cdot\text{HI}\cdot\text{I}_3$, prepared by Jørgensen by exposing a solution of theobromine hydrochloride, mixed with potassium iodide, to the air. By varying the amounts of hydrochloric and hydriodic acids present, the author has obtained compounds having the formulæ—

$(\text{C}_7\text{H}_8\text{N}_4\text{O}_2)_2\text{HI}\cdot\text{HCl}\cdot\text{I}_2$ and $(\text{C}_7\text{H}_8\text{N}_4\text{O}_2)_3\text{HI}(\text{HCl})_2\text{I}_3$, and by re-crystallisation of a mixture of the three from weak alcohol containing hydriodic acid and iodine, a substance of the composition $(\text{C}_7\text{H}_8\text{N}_4\text{O}_2\text{HI})_2 + \text{H}_2\text{O}$ was obtained.

A solution of theobromine in saturated hydriodic acid deposited on standing crystals having the composition $(\text{C}_7\text{H}_8\text{N}_4\text{O}_2\text{HI})_2\text{I}_3$.

131. "A Synthesis of Diphenyloxytriazoline." By GEORGE YOUNG, Ph.D.

The reaction between benzaldehyd and phenylsemicarbazide described in a previous notice (*Proc. Chem. Soc.*, 1894, 95, 124), and represented by the equation $\text{C}_7\text{H}_9\text{N}_3\text{O} + \text{C}_7\text{H}_6\text{O} + \text{O} = \text{C}_{14}\text{H}_{11}\text{N}_3\text{O} + 2\text{H}_2\text{O}$, is shown in the present paper to take place in the following two stages:—I. $\text{C}_7\text{H}_9\text{N}_3\text{O} + \text{O} = \text{C}_7\text{H}_7\text{N}_3\text{O} + \text{H}_2\text{O}$; II. $\text{C}_7\text{H}_7\text{N}_3\text{O} + \text{C}_7\text{H}_6\text{O} = \text{C}_{14}\text{H}_{11}\text{N}_3\text{O} + \text{H}_2\text{O}$. The intermediate product, $\text{C}_7\text{H}_7\text{N}_3\text{O}$, is phenylazocarbonamide, $\text{C}_6\text{H}_5\text{N}:\text{N}\cdot\text{CO}\cdot\text{NH}_2$. It is formed immediately by the action of ferric chloride in aqueous solution, or potassium permanganate in dilute sulphuric acid. It is also formed, but very slowly, by the action of moist air on phenylsemicarbazide. It forms red needle-shaped crystals, m. p. 114° . The second stage of the above reaction does not take place so easily when the intermediate product is isolated as when the benzaldehyd is added to the phenylsemicarbazide before oxidation. In the latter case, the whole reaction takes place in boiling alcohol; in the former, the azo-derivative and the benzaldehyd require to be heated in alcohol in a sealed tube at 120°C . The benzoyl-derivative,—



has been prepared, in addition to those previously mentioned, by the action of benzoyl chloride on diphenyloxytriazoline and its silver salt. It forms flat needles, m. p. 133.5° .

132. "Notes on Piperovatine." By WYNDHAM R. DUNSTAN, F.R.S., and FRANCIS H. CARR.

The method previously used (*Trans.*, 1895) for extracting piperovatine from *Piper ovatum* being exceedingly tedious, the authors experimented with the view of finding a better method. The following process is a considerable improvement, and with its aid the active constituent can now be extracted and crystallised in the course of a few hours. The method consists in percolating with ether; the dark-coloured extract thus obtained is freed from ether and the adhering volatile oil, and then extracted with hot dilute alcohol (13 per cent); on cooling this extract, crystals separate, which may be re-crystallised from 40 per cent alcohol.

Further experiments have been made on the hydrolysis of piperovatine with the small remaining quantity of material. A small quantity was heated with water in a sealed tube to 160°, with the result that a volatile base, probably a pyridine derivative, a substance smelling like anisol and giving phenol, on treatment with sodium hydroxide, and also an acid were produced.

133. "*Dibenzacanine and Tetracetylacanine.*" By WYNDHAM R. DUNSTAN, F.R.S., and FRANCIS H. CARR.

The authors having failed so far to produce aconitine by the acetylation of benzacanine have tried to form benzacanine by introducing a benzoyl group into aconine; this, however, has not yet been contrived, but new aconine derivatives have been obtained. When equimolecular proportions of aconine and benzoic anhydride are dissolved together in chloroform and allowed to stand at the ordinary temperature, reaction occurs with production of dibenzacanine.

Dibenzacanine, $C_{24}H_{37}(Bz)_2NO_{10}$, is unlike aconine in being insoluble in water and soluble in ether; it crystallises from ether in rosettes of needles, m. p. 265°. *Dibenzacanine hydrobromide* crystallises well from a mixture of alcohol and ether, m. p. 261°. *Dibenzacanine aurichloride* is precipitated by adding a solution of gold chloride to a solution of the hydrochloride of the base, and may be crystallised in yellow tables from a mixture of alcohol, ether, and petroleum, m. p. 212°. This salt contained 18.2 per cent of gold; calculated for $C_{24}H_{37}(Bz)_2NO_{10}HAuCl_4$, 18.71 per cent. Hydrolysis of the base furnished 33.3 per cent of benzoic acid; the calculated quantity for $C_{24}H_{37}(Bz)_2NO_{10}$ is 34.4 per cent.

By the action of a large excess of benzoic anhydride, a crystalline base, m. p. 190°, soluble in ether and insoluble in water, is formed, which has not been further examined. Benzoyl chloride dissolved in chloroform does not react with aconine even when heated with the base.

Tetracetyl-aconine is formed when a solution of aconine hydrochloride and acetyl chloride in chloroform is allowed to stand for thirty-six hours at the ordinary temperature. It is insoluble in water, but readily soluble in ether and in alcohol, from either of which solvents it crystallises in small prisms, m. p. 196°.

On hydrolysis, aconine and 35.2 per cent of acetic acid are formed, the formula $C_{24}H_{35}(Ac)_4NO_{10}$ demands 35.8 per cent of acetic acid.

134. "*Molecular Volume Change during the Formation of Dilute Solutions in Organic Liquids.*" By A. WENTWORTH JONES, M.A.

The author has determined the volume changes during the formation of several solutions in benzene and carbon disulphide, and calculated the molecular volume change as $v \times m \times W/V \times M \times w = x$.

Where v = observed volume change,
 V = volume of solution,
 m = molecular weight of substance,
 w = weight of substance taken,
 W = " solvent "
 M = molecular weight of solvent,
and x = " expansion or contraction.

The values for molecular weights of several "non-associating" liquids are very different, and sometimes change their sign, and if the phenomena of these solutions in organic liquids are comparable with those of aqueous solutions of organic compounds, it is impossible to admit that these volume changes are measurements of the attraction of substance for solvent and equal for molecular weights of different substances, as is stated by Traube (*Ber.*, 1895, xxviii., 410).

The author suggests that these volume changes occurring on solution are of the same nature as the smaller changes occurring when a moderately strong solution is diluted, and that both are analogous to the deviations from Boyle's law observed in the case of gases.

The following values have been obtained by the use of the specific gravity method:—

Carbon Disulphide Solutions at 15° C.		Benzene Solutions at 15° C.	
	Molecular expansion.		Molecular expansion.
Methyl formate	0.0797	Methyl formate	0.0156
Ethyl acetate ..	0.0809	Ethyl acetate ..	0.0076
Ethyl acetoacetate	0.1072	Ethyl acetoacetate	0.0120
Paraldehyd ..	0.0972	Paraldehyd ..	0.0141
Nitrobenzene ..	0.0349	Nitrobenzene ..	-0.0040
Benzaldehyd ..	0.0305	Benzaldehyd ..	-0.0042
Aniline	0.0310	Aniline	-0.0067
Benzene	0.0320	Carbon disulphide ..	0.0188
Ethyl iodide ..	-0.0632	Piperidine ..	0.0020
Phosphorus trichloride . .	-0.0913	Phosphorus trichloride . .	0.0041
A contraction occurs in the last two.		A contraction occurs in the 5th, 6th, and 7th cases.	

NOTICES OF BOOKS.

Milk, its Nature and Composition: a Handbook on the Chemistry and Bacteriology of Milk, Butter, and Cheese. By C. M. AIKMAN, M.A., D.Sc. Crown 8vo. Pp. 180. London: A. and C. Black. 1895.

A TREATISE ON milk, as a commercial article of food, without a notice of the bacteria which affect its preservation, modify its properties, and in some cases serve as a *materies morbi*, would in these days be rightly set aside as comparatively worthless. Dr. Aikman has therefore done well to devote a chapter to the bacteria of milk, and elsewhere to notice the presence and the influence of micro-organisms on butter and cheese.

We find here, in the first place, an account of the structure of the cow's udder and of the secretion of milk. Dr. Aikman refutes the old theory that milk is filtered blood. He points out the important chemical difference that sodium salts predominate in the blood, whilst potassium salts are more abundant in milk.

An important chapter is devoted to the percentage composition of milk. A table shows the variation in the composition of cows' milk, as determined by different authorities. The average of fat in the German samples is, according to Fleischman, 3.40; according to Kirchner, 3.4; whilst in American samples it is 4.00; and in English milks the average of 120,540 samples is, according to Vieth, 4.10.

Milk, the author rightly holds, should be defined under a Sale of Foods Act as the "normal secretion of the mammary glands of the cow, and that a person selling *abnormal* milk should be treated as a sophisticator."

The official standard in England is only 3 per cent, whilst in Massachusetts it is 3.70, in Vermont 3.25, and in Philadelphia 3.50.

The three largest mineral constituents found in milk are potash, lime, and phosphoric acid, each forming from 20 to 26 per cent of the total ash.

The fat in the milk of different herds of cows varies no little. In the milk of short-horns it is 3.73, in Jerseys 5.02, in Guernseys 4.90, and in Ayrshires 4.15. We have not been able to meet with an analysis of a trustworthy specimen of the milk of Lancashire long-horns, but we believe it is at least as rich in fat as that of the Ayrshires.

Dr. Aikman does not accept the view that the richness of a milk in fat is shown by the depth of the layer of cream. He rejects the belief that thunder turns milk sour.

On the importance of cleanliness in every department of the milk trade the author insists most emphatically, showing how the hands of milkmen, the teats of cows, and the milk pails become rapidly contaminated.

The importance of milk as a vehicle of various diseases is carefully shown. Tuberculosis, typhus, diphtheria, and cholera are thus conveyed. According to Hart, of fifty epidemics of typhus investigated in England, twenty-eight were traced to infected milk.

We cannot prolong our survey of this valuable work, but we can conscientiously recommend it to all persons connected with the milk industries.

The Handling of Dangerous Goods: a Handbook for the Use of Government and Railway Officials, Carriers, Shipowners, Insurance Companies, Manufacturers and Users of such Goods, and others. By H. JOSHUA PHILLIPS, F.I.C., F.C.S. Crown 8vo., pp. 362. London: Crosby Lockwood and Son. 1895.

THE number of substances dangerous from one or other point of view which are met with in modern commerce is great. As a consequence, accidents to property and to human life are constantly occurring, due sometimes to the ignorance or the recklessness of manufacturers and merchants, and perhaps more frequently to the negligence of their servants. Hence Mr. Phillips has done well in presenting the public with the work before us. He is already favourably known to many of our readers by his works on "Engineering Chemistry" and on "Fuels, their Analysis and Valuation," and in his former capacity as consulting chemist to the Great Western and Great Eastern Railways he has enjoyed special opportunities of studying the classes of goods here under consideration.

The first part of the book treats successively of combustible acids, alkalies, salts, and gases, of coal-tar and its products, of petroleum and its products, of fixed oils and fats, of volatile oils and of various highly inflammable liquids, of inflammable solids, of substances liable to spontaneous combustion, and of explosives. These chapters are exceedingly well written, and, if duly studied and aided upon by the interests concerned, will be productive of much good. Some substances, however, are mentioned which are of little importance, such as vasolene. As for roasted and ground coffee, their importation and carriage by railway, if it ever occurs, is an evil; and as for date-stones and olive-kernels, they should never be allowed to be landed. The author does not mention ground dye-woods, the storage of which is often dangerous. Worst of all substances liable to spontaneous combustion are weighted or loaded silks, of which Insurance Companies should beware. The methods laid down for ascertaining the safety of explosives are those in practical use.

The Explosives Act of 1875 is here given at some length, together with the comments of Sir F. Abel. In some cases the penalties enacted for the offences against the provisions of the Act are unreasonably low.

The second part of the work narrates a series of accidents which are well named "instruative," and which may serve as a salutary lesson to persons who have to handle dangerous goods. It appears, from the Bombay calamity of 1891, that blasting gelatin is—especially in hot climates—liable to spontaneous decomposition. The dynamite catastrophe of Santander (1893) seems to show that the possible gains derived from high explosives are not enough to compensate for their evil results.

The number of accidents from mineral oil lamps is alarming, and it is especially to be regretted that such lamps while burning are frequently thrown at each other by persons quarrelling.

The intentional outrages effected in many cases by "Atlas powder A" exhibit a black record. Here, also, the perpetrators when detected too often escape with inadequate punishment.

The third part of the work gives the special railway classification, mode of packing, &c., for the conveyance of explosives by goods trains. Some of these classifications are open to objections.

An Appendix, containing a variety of useful tables, concludes the work.

The "Handling of Dangerous Goods" merits a wide circulation, and an intelligent, appreciative study.

Laboratory Manual of Inorganic Preparations. By H. T. VULTE and GEORGE M. S. NEUSTADT. New York: 1895. Pp. ii., 180, iii. 12 mo., ill.

THE authors of this useful handbook observe that the study of organic chemistry is usually conducted on a more logical plan than that of inorganic, synthetic work preceding analytical, and researches, and they propose that this work should be placed in the hands of students before they begin the study of analytical chemistry. It shows "how compounds, often very complex in character, rare in occurrence or expensive in preparation, may be produced from simple substances, or from those which are comparatively plenty and cheap, and how the by-products may be saved." The substances to which the attention of the student is directed embrace water (ammonium-free), ethyl-alcohol, oxygen, hydrogen, nitrogen, chlorine, hydrochloric acid, nitric acid, nitrous oxide, and after several other mineral acids and oxides, compounds of calcium, lead, bismuth, of the alkalies, &c., as well as hydroxylamine, hydrazine, chydrazine, and carbonoxysulphide.

The instructions for preparing all these substances are clearly worded; perhaps the quantities taken are unnecessarily large in some cases, but this is a minor fault. References to original papers are often introduced, and equations expressing reactions are generally given when advisable.

In certain instances it is difficult to understand the reasons for selecting a given substance for study; but this remark would apply to any work of similar character, unless the reviewer happened to be the author as well.

The authors generally place the chemical formula of the substance under discussion at the head of each section, but not uniformly; they have taken pains to inform the student that hydrochloric acid has the formula HCl, but they neglect to inform him as to the composition of hydrazine, and of platinoso-chlorides, bodies presumably less known.

The work has an index, but lacks a table of contents.

The first-named of the authors has had experience in teaching large classes in the School of Mines, Columbia College, and undoubtedly knows the needs of students beginning the study of chemistry.

The handbook can be cordially recommended.—H. C. B.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxi., No. 20, November 11, 1895.

On Tempering Extra-Hard Steels.—F. Osmond.—If we take an ingot of steel carburized by cementation in which the proportion of carbon varies in a continuous manner from end to end (say from 1.70 to 0.35 per cent), submit it to very energetic tempering, and then try with a sewing needle to scratch a polished surface, we find, as might be expected, that the needle scratches the softest

parts up to about 0.70 per cent; the mark is then interrupted, but, contrary to all received ideas, it re-appears when the proportion of carbon exceeds 1.30 per cent. On examining this scratch in the most highly carburetted parts with the microscope it is found to be not continuous, but presents frequent interruptions. The region in question is therefore not homogeneous, and contains at least two constituents which we may call A and B. A, which is not scratched by the needle, scratches glass and orthose; B is scratched by apatite and perhaps by fluor-spar. A has a slight greyish tint, whilst B is of a silvery whiteness.

On Nickel and Cobalt Silicides.—M. Vigouroux. —M. Moissan has recently made known the action of silicon upon iron, chromium, and silver. The author now describes nickel and cobalt silicides obtained in a similar manner. These silicides have a distinctly metallic aspect and a steel-grey colour perfectly crystalline. Nickel silicide has a specific gravity of 7.2 at 17°; cobalt silicide is 7.1 at the same temperature. They are more easily fusible than silicon or than the pure metals, but they resist the highest temperatures without decomposition. Fluorine attacks them with incandescence at the ordinary temperature. In dry chlorine they burn with incandescence at a red heat. The composition of the nickel compound is SiNi_2 , and that of the cobalt silicide is analogous.

On the Alcoholates.—H. Lescœur.—The author describes the compounds $\text{C}_2\text{H}_5\text{NaO}_2\text{C}_2\text{H}_5\text{O}$, $\text{C}_2\text{H}_5\text{N}_2\text{O}$, NaHO , $\text{C}_2\text{H}_5\text{O}$, and NaHO , $3\text{C}_2\text{H}_5\text{O}$.

Properties of the Emulsine of Mushrooms.—Em. Bourquelot and H. Hérissay.—One and the same emulsine appears to exist in the mushrooms, but we have as yet no evidence that it differs from the emulsine of almonds.

Constancy of the Congelation-point of some Liquids of the Organism.—J. Winter.—As regards milk the constancy of its congelation-point seems to me to afford a simple and certain check on its state of purity. This study reveals to us a novel and unknown function of the blood-globules or of the fibrine.

Fermentations induced by Friedland's Pneumobacillus.—L. Grimbart.—The author's pneumobacillus differs from that of Frankland by its property of attacking glycerin and dulcitol, by the nature of its fermentation-products, and by the energy of its action.

Direct Fixation of certain Metallic Oxides by Vegetable Fibres.—A. Bonnet.—The author finds that the copper, zinc, cobalt, and iron (ferric) hydroxides may be directly fixed upon vegetable fibres in conditions similar to those observed with the lead oxides.

Zeitschrift für Anorganische Chemie,
Vol. viii., Part 6.

Occlusion of Barium Chloride by Barium Sulphate.—T. W. Richards and H. G. Parker.—The occlusion of barium chloride by barium sulphate occasions considerable errors. The occlusion is greater in concentrated than in dilute solutions, greater in presence than in the absence of hydrochloric acid, and greater if the sulphate is added to the barium than in the inverse case. In the ordinary conditions of careful precipitation in presence of a slight quantity of free acid, the error occasioned by occlusion is nearly compensated by the solubility of barium sulphate in water or acids; this solubility must be taken into account in careful determinations. The error occasioned by occlusion can be corrected with great accuracy if the chlorine retained by the precipitate is determined and the corresponding weight of barium chloride is deducted from the total weight of the precipitate.

Colour, Specific Gravity, and Surface Tension of Hydrogen Peroxide.—W. Spring.—Hydrogen peroxide

is a liquid of the same colour as water, though of a darker shade. Its specific gravity is 1.4996 and its surface tension smaller than that of water by more than one-half—3.582 as against 7.750. The colour which is shown by oxygen, in a higher degree by ozone, reappears in water and in hydrogen peroxide. All the facts seem to show that in H_2O_2 the oxygen has lost its characteristic attributes to a less extent than in H_2O . In a word, hydrogen peroxide seems in a chemical point of view to be rather a non-saturated compound between O_2 and H_2 than a true atomic compound. Hydrogen peroxide in a pure dry state decomposes no less violently than nitrogen chloride or nitro-glycerin.

Atomic Weight of Molybdenum.—Karl Seubert and William Pollard.—The authors find from molybdenum trioxide by the acidimetric process $\text{Mo}=95.729$, and by the reduction of the trioxide to metal $\text{Mo}=95.735$. The results of Dumas, Debray, Liechti and Kempe, Smith and Maas, and Seubert and Pollard yield a mean of 95.77, or if he bear in mind the uncertainty of the second decimal, $\text{Mo}=95.8$.

Heavy Metallic Salts of Bichromic Acid.—Gerhard Krües and Oskar Unger.—The authors did not succeed in obtaining bichromates of the heavy metals in a definite form, but were merely able to produce crystalline double salts of metallic and alkali bichromates. The bichromates of the heavy metals are in general not capable of crystallisation.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. x., No. 118.

The Smokeless Pyro-collodion Powder of Prof. Mendeleeff.—This lengthy paper does not admit of abstraction. It concludes with the well-known dictum: *Si vis pacem para bellum*.

Industrial Preparation of Liquid Air and Oxygen by means of the Linde Process.—This memoir requires the accompanying figures and the table of curves.

Tar of Naphtha.—This paper does not admit of useful abridgment.

MISCELLANEOUS.

Royal Society.—The following President, Officers, and Council were elected on November 30th last:—

President—Sir Joseph Lister, Bart., F.R.C.S., D.C.L.

Treasurer—Sir John Evans, K.C.B., D.C.L., LL.D.

Secretaries—Prof. Michael Foster, M.A., M.D.; The Lord Rayleigh, M.A., D.C.L.

Foreign Secretary—Edward Frankland, D.C.L., LL.D.

Other Members of the Council—William Crookes, F.C.S.; Sir Joseph Fayrer, K.C.S.I.; Lazarus Fletcher, M.A.; Walter Holbrook Gaskell, M.D.; William Huggins, D.C.L.; The Lord Kelvin, D.C.L.; Prof. Alexander B. W. Kennedy, LL.D.; Prof. Horace Lamb, M.A.; Prof. Edwin Ray Lankester, M.A.; Prof. Charles Lapworth, LL.D.; Major Percy Alexander MacMahon, R.A.; Prof. John Henry Poynting, D.Sc.; Prof. Arthur William Rücker, M.A.; Osbert Salvin, M.A.; Prof. Harry Marshall Ward, D.Sc.; Admiral William James Lloyd Wharton, C.B.

Royal Institution.—The following are the Lecture Arrangements before Easter:—Professor John Gray McKendrick, Professor of Physiology in the University of Glasgow, Six Lectures (adapted to a juvenile auditory) "On Sound, Hearing, and Speech" (experimentally illustrated); Professor Charles Stewart, Fullerton Professor of Physiology, R.I., Eleven Lectures on "The External Covering of Plants and Animals: its Structure and Functions"; The Rev. Philip H. Wicksteed, Four Lectures

on "Dante"; Professor H. Marshall Ward, Professor of Botany in the University of Cambridge, Three Lectures on "Some Aspects of Modern Botany"; The Rev. William Barry, D.D., Four Lectures, "Masters of Modern Thought"—Voltaire, Rousseau, Goethe, and Spinoza; Professor C. Hubert H. Parry, Professor of Musical History and Composition at the Royal College of Music, Three Lectures on "Realism and Idealism in Musical Art" (with musical illustrations); The Right Hon. Lord Rayleigh, Professor of Natural Philosophy, R.I., Six Lectures on "Light." The Friday Evening Meetings will begin on January 17th, when a Discourse will be given by the Right Hon. Lord Rayleigh, on "More about Argon." Succeeding Discourses will probably be given by Professor Burdon Sanderson, Mr. W. S. Lilly, Dr. John Murray, Mr. J. J. Armistead, Dr. Edward Frankland, Mr. A. R. Binnie, Mr. Sidney Lee, Professor T. R. Fraser, Professor Dewar, and other gentlemen.

MEETINGS FOR THE WEEK.

MONDAY, 9th.—Society of Arts, 8. "Mechanical Road Carriages," by H. Worby Beaumont, M. Inst.C.E. (Cantor Lectures).
WEDNESDAY, 11th.—Society of Arts, 8. Adjourned Discussion on Mr. Ounynghame's Paper on "Locomotive Carriages for Common Roads."
FRIDAY, 13th.—Physical, 5. "A Mechanical Device for Performing the Temperature Corrections of Barometers," by Dr. John Shield. "On the Existence of Earth-Air Electrical Currents," by Prof. A. W. Rüchser, F.R.S.

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THE CHEMICAL NEWS.

VOL. LXXII., No. 1881.

ON THE GASES OBTAINED FROM THE MINERAL ELIASITE.

By J. NORMAN LOCKYER, C.B., F.R.S.

OBSERVATIONS have been made of the gases obtained from the mineral eliasite heated *in vacuo*, in the manner which I have described in a former paper (*Roy. Soc. Proc.*, lviii., p. 68), and, in addition to lines of known gases, others have been noted, for which no origins can be traced, at the following wave-lengths:—

Angström.	Rowland.
6121'2	6122'4
6064'5	6065'7
5990'0	5991'6
5874'9	5875'9 (D ₃)
5845'7	5846'8
5428'8	5429'9
5403'1	5404'1

The wave-lengths of these lines have been determined by means of a Steinheil spectroscope having four prisms, comparisons being made with adjacent metallic lines, and the positions interpolated by micrometric measurements; the accuracy may perhaps be taken to be within 0'1 tenth metres. Other lines have been noted, but are not included in the list, for the reason that their wave-lengths have not yet been determined with the dispersion stated above.

Of the lines in the foregoing list, six are in all probability coincident with chromospheric lines, as shown in the following table, which also indicates the frequencies and brightnesses of the lines according to Young:—

Wave-length of Chromospheric Lines.

(Angström's scale).	(Rowland's scale).	Frequency.	Brightness.
6121'2	6122'4	5	3
6064'5	6065'7	5	2
5990'0	5991'6	10	4
5874'9 (D ₃)	5875'9	100	90
5428'8	5429'9	8	3
5403'1	5404'1	5	3

It is important to point out that all these lines do not appear in the spectrum at the same time. For instance, in the first two specimens of the mineral no trace of D₃ was noted, but in the third portion examined, all coming from the same specimen, D₃ appeared as a pretty bright line. Again, as in the case of a previous operation on bröggerite (*Roy. Soc. Proc.* lviii., p. 194), in one experiment with eliasite the products of distillation, collected in four stages, gave different spectra.

These facts seem to indicate that the gas obtained from eliasite is either a compound or a mixture of gases, just as is that obtained from bröggerite according to former experiments.

It is also to be remarked that among the lines in the eliasite spectrum, those at 6122'4 and 6065'7 have been recorded in the gases obtained from clèveite, and 6122'4 has also been noted in the gas obtained from gummite.

It seems to me more than probable, therefore, that the lines observed in eliasite indicate a new gas, in some way associated with those given off by clèveite and bröggerite,

and the fact that D₃ is not necessarily present in the spectrum furnishes an additional argument in favour of the view that the gas obtained from clèveite or bröggerite is complex.

THE HISTORY OF MOND'S NICKEL EXTRACTION PROCESS.*

By LUDWIG MOND.

IN the present paper I give an account of the history of my process of extracting nickel from its ores, as an instance of an investigation undertaken in pursuit of pure science, which has led unexpectedly, in a few years, to an important industrial application. I have often been asked by scientific men how I came to discover nickel carbonyl, and can now explain. Soon after I had satisfied myself that the ammonia soda process was far cheaper than the Leblanc process for producing carbonate of soda, it became evident to me that a time would come when the Leblanc process would produce carbonate of soda, as a by-product of the bleaching powder manufacture, which it would have to dispose of at any price it would fetch. I therefore undertook a series of experiments, with the object of producing bleaching powder as a by-product of the ammonia soda process. You all know that the usual form of this process consists in treating a solution of common salt in which caustic ammonia has been dissolved by carbonic acid, with the result that bicarbonate of soda is precipitated, while a solution of ammonium chloride is formed. In the ordinary course of things this solution of chloride of ammonium is distilled with caustic lime, yielding gaseous ammonia, which returns to the process and a solution of calcium chloride. Other investigators had endeavoured to produce chlorine from the chloride of calcium obtained by evaporating these solutions; others have proposed to substitute magnesia for the lime in distilling the solution of ammonia chloride, and to produce chlorine or hydrochloric acid from the MgCl₂ obtained by evaporating its solution. I gave my attention to producing the chlorine direct from the ammonium chloride, separated from the solution in which it is originally obtained by refrigeration.

Ammonium chloride when vapourised is, as is well known, dissociated into ammonia and H₂Cl; thus, if the vapour of NH₄Cl is passed over a metallic oxide, this oxide is converted into a chloride and the ammonia passes on altogether with the steam formed by the reaction.

I found that nearly all metallic oxides, with the exception of the alkalis and alkaline earths, and that even a large number of metallic salts, were acted upon in this way by NH₄Cl vapour, and that a large number of the metallic chlorides so formed would give up their chlorine by re-converting them into oxides by submitting them to the action of the air at a suitable temperature. I found that, of all the substances investigated, oxide of nickel yielded the best results, and that the next best were obtained by magnesia mixed with a certain amount of chloride of potassium.

In developing this process I had to construct a plant for volatilising NH₄Cl, which I found an extremely difficult problem, as the vapour of this substance not only acts on oxides and salts, but also violently attacks the large majority of metals. I succeeded in lining iron vessels with glazed tiles in such a way that they would withstand this action, but I required valves for changing from the current of ammonium chloride vapour to hot air, and *vice versa*, which had to be very tight to prevent a large loss of ammonia. I found that nickel was one of the few substances suitable for the construction of these valves, and that it was not at all attacked by ammonium chloride vapour.

* A Paper read before the Royal Society, November 21, 1895.

* Abstract of Paper read before the New York section of the Society of Chemical Industry.

These worked perfectly on a laboratory scale, but when applied on a manufacturing scale they became leaky, and the faces became covered with a black crust, which on examination was found to contain carbon. The source of this carbon seemed mysterious; the only difference between the work on the small scale and that on the large was that on the small scale we swept the ammonia out of the apparatus before admitting the hot air by means of pure CO_2 , while on the large scale we used the gases from the lime-kiln containing a few per cent of CO. We found nickel to have the remarkable property of splitting off carbon from CO at a moderate heat, transforming it into CO_2 .

In the course of the experiments finely divided nickel, formed by reducing nickel oxide at 400°C . by hydrogen, was treated with pure CO in a glass tube at varying temperatures for a number of days, and was then cooled down in a current of CO before it was removed from the tube. In order to keep the poisonous CO out of the atmosphere of the laboratory we simply lit the gas escaping from the apparatus. To our surprise we found that, while the apparatus was cooling down, the flame of the escaping gas became luminous, and increased in luminosity as the temperature got below 100°C . On a cold plate of porcelain put into this luminous flame, metallic spots were deposited, similar to the spots of arsenic obtained with the March apparatus, and on heating the tube through which the gas was escaping we obtained a metallic mirror while the luminosity disappeared. Upon examination of the mirrors we found them to consist of pure nickel. As it seemed improbable that so heavy a metal as nickel should form a readily volatile compound with CO we purified our CO as perfectly as possible, but still obtained the same results.

We now endeavoured to isolate this curious and interesting substance by preparing the nickel with great care at the lowest possible temperature, and treating it with CO at about 50°C ., and thus we greatly increased the amount of the volatile nickel compound in the gases passing through the apparatus. We observed the excess of CO by cuprous chloride solution, and thus obtained a residue of several c.c. containing the volatile nickel compound mixed with a little nitrogen. By passing this gas through a heated tube we separated the nickel and obtained an increased flame of gas, and found in this a quantity of CO corresponding to about four equivalents for one equivalent of nickel. By further improving our method of preparing the finely divided nickel, and by passing the resulting gas through a refrigerator cooled by snow and salt, we at last succeeded in liquefying this compound, and were able to produce it with ease and facility in any quantity we desired.

This nickel carbonyl is a colourless liquid, boiling at 43°C ., and which solidifies at -25°C ., forming needle-shaped crystals. It is soluble in alcohol, petroleum, and chloroform; it is not acted upon by dilute acids or alkalis, and can be readily distilled without decomposition. But on heating the gas to 150°C ., it is completely dissociated into its components, pure CO being obtained and the nickel being deposited in a dense metallic film upon the sides of the vessel in which it is heated.

After continued investigation I came to the conclusion that it ought to be possible to make use of the ease with which nickel is converted into a volatile gas by CO for separating nickel from cobalt and other metals on a manufacturing scale, and for obtaining it in a very pure state. We have now succeeded in producing nickel at the rate of 14 tons per week, from the Canadian nickel matte imported into England. We erected a plant near Birmingham for this purpose. This matte, which contains about 40 per cent nickel and an equal quantity of copper, is carefully roasted, to drive out the sulphur as far as possible, and is then subjected to the action of hydrogenous gases, either water gas or producer gas rich in hydrogen, in an apparatus which is called the "reducer," the temperature of which is under perfect control, so that 400°C .

is never exceeded. From this apparatus the substance which is now reduced to the metallic state is taken, through air-tight conveyors and elevators, into another apparatus called the "volatiliser," in which it is subjected, at a temperature not exceeding 80°C ., to the action of CO gas. This apparatus consists of an iron cylinder divided into numerous compartments by shelves, and provided with a stirring device which moves the material from the top to the bottom, while the CO gas passes through in an opposite direction. The CO gas, which should be as rich as practicable, we prepared by passing pure CO_2 through incandescent coke; the pure CO_2 we make by passing the flue gas of a boiler or of a fire through a solution of carbonate of potash, and subsequently boiling the solution. The CO gas, charged with nickel carbonyl leaving the volatiliser, is passed through a series of tubes or chambers heated to about 180°C ., in which the nickel is deposited in various forms, according to the speed of the gas current, the richness of the gas, and the existing temperature. The CO gas, thus almost completely free from the nickel, is taken back by means of a blower into the volatiliser, where it takes up a fresh quantity of nickel, and is constantly used over and over, so that the quantity consumed is limited to the very small amount of unavoidable loss through leakage of the plant.

The material under treatment is repeatedly dumped from the volatiliser to the reducer, and *vice versa*, by means of air-tight conveyors and elevators, until the amount of nickel volatilised begins to fall off. It is then roasted again, to remove the sulphur which it still contains, and is treated by sulphuric acid to dissolve part of the copper. The remaining mass, containing all the nickel, some copper, and the other impurities of the matte, is again subjected to the previous treatment until the nickel has been extracted as far as practicable, and the ultimate residue, still containing a few percentage of nickel, is melted up into matte again.

If the nickel is allowed to deposit slowly, at a carefully regulated temperature, it can easily be obtained from the gas as a coherent metallic film, so that it is possible to coat any substance which can stand heating to 150°C . with a perfect covering of metallic nickel, and also to make articles of metallic nickel for direct use.

Hollow nickel goods can be made in this way, which at present either cannot be made at all or only by the use of very powerful hydraulic machinery, and this will give a great impetus to the manufacture of nickel utensils for domestic purposes, the use of which is so very desirable from a sanitary point of view. The cost of the process, if carried out on a sufficiently large scale, is inconsiderable.—*Engineering and Mining Journal*.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 276).

CHAPTER III.

CHEMICAL RESEARCHES ON THE CHLORIDE, CHLORATE, PERCHLORATE, AND CHLOROPLATINATE OF POTASSIUM.*

Introduction.

ACCORDING to my experience up to the present, the molecular weight of chloride of potassium does not agree with Prout's hypothesis. Does this depend on the fact that the atomic weight of potassium is not a simple ratio of that of metallic silver which is used as the standard for comparison; or is it rather due to accidental impurities which might be in the chloride tested; or is it, lastly, that

* This research was commenced in the month of December, 1876, and completed in 1883.

potassium is not an element? Such is the problem I endeavoured to solve by re-opening the study of chloride of potassium, which had already been the subject of lengthy investigations on my part.

In my *New researches on the laws of chemical proportions* I said "I must admit then that I could not prepare, by means of chlorate of potassium, a chloride which I could consider absolutely pure." In fact, after having successively eliminated the foreign matters contained in the purest chlorate of potassium, I detected, in the chloride made from it, the presence of silicon in the form of silica and alkaline silicates, and amongst them silicate of sodium in various quantities according to the conditions under which the chloride was produced. The total weight of silica and alkaline silicates was as much as 1-20,000th of the whole. When changing this chloride into chloroplatinate of potassium, I was able to decrease to one-half the weight of the residue left by volatilising chloride of potassium. As far as regards the silica and alkaline silicates, the minimum limit was then 1-40,000th of the whole. It was impossible for me to tell exactly the quantity of sodium existing in the chloride, or even the state in which the whole of this metal existed. I have always believed that the bulk was in the form of a silicate. Farther on I shall give the reason for this opinion. From my experience I can state that it is not always in the form of sodium chloride. In fact, by using a silver salt, it is possible, and even easy, to ascertain the presence of 1-10,000th part of chloride in a solution of chlorate or perchlorate of potassium in pure water. Now, a solution of these salts in absolutely pure water, which, on spectrum analysis, gives persistent and strong indications of the presence of sodium, remains absolutely clear, and, when exposed to light, *protected from atmospheric dust*, remains colourless, after having received a proper amount of nitrate or sulphate of silver,—a phenomenon which it is not possible to obtain with a solution of chlorate or perchlorate containing 1-10,000th of these salts. Bunsen, moreover, has shown that spectrum analysis discloses an amount of chloride of sodium 300,000 times less than that shown by using silver salts. The failure of chemists to procure, by crystallisation or otherwise, potassium salts which do not show the potassium line when volatilised in a colourless flame or in an electric spark, has led Mr. Lockyer to believe in the splitting up of potassium into sodium and another metal. I do not altogether agree with this hypothesis; the work I describe farther on is for the purpose of seeking what foundation it can have on fact, as much with regard to potassium as to other bodies, such as lithium, calcium, strontium, barium, thallium, silver, mercury, platinum, iridium, &c. Whilst admitting the possibility of procuring chloride of potassium absolutely free from sodium, silica, alkaline silicate, and all other known foreign bodies, what guarantee have we that the metal contained in it is truly an element?

When regarding it from the standpoint of experience actually acquired, there are as many reasons for considering the metallic base of this chloride to be an element as there are for considering the hydrogen in hydrochloric acid to be an undecomposable body. In short, the combinations and decompositions of the metal used in the reactions are always done in such a manner as to reproduce a body identical with itself, when submitted to chemical forces,—quite as powerful, in a different way, as physical forces,—exactly the same as hydrogen, no more, no less. The chloride from chlorate, and the chloride from chloroplatinate of potassium, though formed under very different conditions, are identical in all their properties. By my previous work I know that potassium, though it may form a chlorate, chloroplatinate, nitrate, or tartrate of potassium, is the same; it is represented by a *constant*. I think I am right in concluding, with most chemists, that potassium is as much an undecomposable body as hydrogen.

Wishing, however, to submit this conclusion to a new proof, I have had recourse to a second method of investi-

gation. Before publishing, I beg to say that I had no confidence in the success of my undertaking. The search for knowledge and truth has throughout influenced my work.

If the metal contained in the chloride of potassium, formed by the dissociation of pure chlorate by the action of heat, be a simple undecomposable body, it seemed to me that, when submitting the chlorate to the action of heat, in such a manner as to reduce it partially into oxygen, chloride, and perchlorate of potassium, the proportion of chlorine to metal ought to be invariably the same in the chloride and in the perchlorate formed simultaneously with a similar chloride. The chloride which was made by the formation of perchlorate, and the chloride given off by the subsequent decomposition of this perchlorate, ought to be identical in every respect.

If, on the other hand, the metallic base of pure chlorate of potassium is a compound body, capable of being split up, the chloride and the perchlorate made by the dissociation of pure chlorate of potassium by the action of heat, ought to combine chlorine and the metal in different proportions, and the chloride made at the same time as the perchlorate ought to be different from the chloride made by the decomposition of this perchlorate.

As a matter of fact, chemical reactions do take place in this manner when we submit chlorate of potassium containing chlorate of sodium to the action of a suitable heat. When heating chlorate of potassium, mixed with 5 per cent of its weight of chlorate of sodium, in a platinum vessel, we find, after complete dissociation of the chlorates, nearly all the sodium in it in the form of chloride of sodium, in the resultant chloride of potassium. The platinum vessel is slightly attacked, forming a noticeable amount of chloroplatinate of sodium, as is always the case when one decomposes chlorate of sodium in platinum.

The perchlorate formed at the same time as the chlorides of potassium and sodium, contains only potassium. By a suitable treatment with alcohol, followed by successive crystallisations, repeated sufficiently often, in platinum vessels sheltered from atmospheric sodium, one can make the separation in such a manner as to obtain, on the one hand, chloride of potassium containing all the sodium, and, on the other, a perchlorate of potassium which behaves under spectrum analysis like all potassium perchlorate which has been long in contact with air, or rather in contact with a sodium compound more soluble than itself, and from which one has eliminated—by means of successive crystallisations and washings in alcohol—the sodium salt which was mixed with it.

Now if the metallic base of chlorate of potassium, in such a state of purity as I have been able to prepare it, is a compound body, one can reason by analogy that, by a properly regulated heat, the separation ought to take place in such a manner as to concentrate in the chloride or perchlorate, the whole—or at least a part—of one of the components of the metallic base of the chlorate.

The chemical *constant* of bodies being different, experience shows that the proportion of chlorine to metal in a chloride and a perchlorate ought consequently to be different, and to be between the limits of these constants. For the purpose of ascertaining what the real facts are, I started a long course of investigation.

I tried first whether it was possible to obtain chlorate of potassium which would not show the sodium line, and would be capable of being made to yield a chloride quite free from bodies, whether solid or volatile, foreign to its normal composition. Having had a chance of succeeding in this delicate research for a chlorate containing silica and sodium in the form of silicate of potassium and sodium, I subjected the purified chlorate to the action of heat in such a way as to form at the same time as the chloride:—

1st. The greatest possible quantity of perchlorate.

2nd. A quantity of perchlorate just sufficient to make the chloride necessary for determining its proportional combination with pure silver.

I will describe all these researches and the results at which I arrived as shortly as possible.

On the Methods used to Eliminate the Solid Foreign Bodies generally found in Commercial Chlorate of Potassium.

It follows, from sufficiently well-known facts, that chlorate of potassium purified by means of successive crystallisations to the point of no longer clouding a 10 per cent solution of silver may yet contain iron, manganese, copper, and silver, and always has in it some sodium, aluminium, calcium, and silicon.

Copper and silver are eliminated at once by the addition of a sufficient quantity of sulphide or hydrosulphide of potassium to a saturated solution of chlorate at 100°. At first almost all the iron and manganese remain in solution: they are only precipitated when one keeps the saline solution slightly boiling for from fifteen to thirty minutes; but in this state the liquid, which is alkaline, perceptibly attacks the porcelain or glass dish in which the operation is carried on.

The salt which crystallises out on suddenly cooling the filtered liquid from which the copper and silver have been thus eliminated is often slightly tinted pink. This colour disappears on carefully washing the salt with a solution containing 1-1000th part of hydrosulphide of potassium cooled nearly to zero, followed by a wash in pure iced water. When losing its colour, the chlorate loses the greater part of the iron and manganese, as well as the aluminium, sodium, calcium, and silicon.

On dissolving the salt thus obtained in pure boiling water, to saturation, and on adding to the solution a sufficient quantity of pure hydrosulphide of potassium to give it a strong alkaline reaction, one obtains, on suddenly chilling the filtered liquid, a white, powdery, crystalline chlorate, from which a wash in a solution containing one thousandth part of hydrosulphide of potassium, followed by a second wash in pure iced water, eliminates the remaining iron, manganese, and aluminium, but not all the silicon, sodium, and calcium contained in it. On repeating the dissolving, crystallisation, and washing a great number of times under the same conditions,—that is to say, in porcelain or glass dishes, and in the presence of air containing sodium and silicon,—one can certainly diminish to a great extent the proportion of sodium, calcium, and silicon in the chlorate; but it appears to me that at the fourth treatment one reaches a limit at which the porcelain or glass dishes, and the surrounding air, supply as much silica, sodium, and calcium as the treatment suffices to eliminate.

After the third treatment one is therefore obliged to work in platinum vessels of a proper shape, and in air enclosed and purified. By acting thus, I have been able, by six successive crystallisations, of which the last three were in platinum, to obtain chlorate quite free from silicon, from all solid bodies whatever, and from sodium, provided this metal exists entirely in the raw chlorate in the form of silicate of sodium, as has been the case in all the samples of chlorate, save one, supplied to me. If, on the other hand, the sodium contained in it is partially in the form of sodium chlorate, there is a limit which one cannot practically pass, so long as one causes the separation of the silica by means of sulphide, or hydrosulphide of potassium, or potash, in addition to carefully washing the crystals with alcohol, in enclosed air.

I have tried this method of eliminating from chloride, sulphate, and nitrate of potassium, the silicon, aluminium, and calcium, which are nearly always met with in these compounds when purified by successive crystallisations.

With proper care, the elimination of these bodies is very easy, especially sulphate of potassium. After five successive crystallisations, of which the last three were effected in platinum and in air enclosed and purified, I

have succeeded in obtaining a sulphate and a nitrate which, when warmed with just enough pure sal ammoniac, formed a chloride which volatilised without leaving a trace of solid residue. This study enabled me to prove that after the elimination of silicon, aluminium, and calcium, the sulphate, nitrate, and chloride still retain sodium, the chloride and nitrate in very minute quantities, the sulphate, on the other hand, in comparatively large quantities,—an evident proof that, in the compounds submitted to purification, the metal sodium existed respectively in the forms of sulphate, nitrate, and chloride. I repeat that the use of sulphide, hydrosulphide, and hydroxide, to catch the sodium, is only effective provided this metal is in the potassium salt exclusively as a silicate.*

I describe farther on, with necessary details, the preparation of the chlorate, perchlorate, and chloride of potassium used in my researches.

(To be continued).

ON THE TECHNICAL ANALYSIS OF CYANIDE WORKING SOLUTIONS.†

By W. BETTEL.

FOR some time past I have felt the need of some quick method of analysis which would in a reasonable time give the composition of working cyanide solutions, so that the chemist-in-charge, or the foreman, in a cyanide works, could trace to its source any irregularity in the working of such solutions with a view to its correction. After many fruitless trials I have pleasure in drawing your attention to some volumetric processes, which, although not all that could be desired, are still sufficiently accurate to be used for technical work, and have this advantage, that the work may be performed by men who have not had the advantage of a technical or scientific training. I do not lay claim to any novelty in this analytical process, it is merely pieced up from well known analytical methods and chemical reactions; but, nevertheless, I hope it will be useful to those of our members who have to examine cyanide solutions.

It is necessary to state at the outset that my remarks have reference to the MacArthur-Forrest working solutions containing zinc, an element which complicates the analysis in a truly surprising manner. Before dealing with the analysis proper, I will draw your attention to the peculiarities of a solution of the double cyanide of zinc and potassium, usually written K_2ZnCy_4 . As is stated in works on chemistry, this cyanide is alkaline to indicators. Now here lies the peculiarity. To phenolphthalein the alkalinity, as tested by N/10 acid, is equal to 19.5 parts of cyanide of potassium out of a possible 130.2 parts. With methyl-orange as indicator, the whole of the metallic cyanide may be decomposed by N/10 acid, as under:—



On titration with nitrate of silver solution the end-reaction is painfully indefinite. If caustic alkali in excess (a few c.c. normal soda) be added to a known quantity of potassic

* I am certain that the principle involved in eliminating the silica and aluminium always contained in chlorate of potassium crystallised from pure water, by means of crystallisations made in water rendered alkaline by potash or hydrosulphide of potassium, is applicable to the elimination of the silica and aluminium contained in sulphate of sodium crystallised in pure water. By transforming sulphate thus purified, by means of chloride of ammonium, I have obtained chloride of sodium capable of being volatilised without leaving a trace of residue,—a thing I had not previously succeeded in doing. In future, one will be able to use the proportional combination with silver and chloride of sodium, and ascertain, without hypothesis, whether the atomic weight of silver and the molecular weight of chloride of sodium are integral multiples of that of hydrogen.—January, 1896.

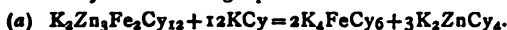
† A Paper read before the Chemical and Metallurgical Society, Johannesburg, S.A.R., August, 1895.

zinc cyanide solution together with a few drops of potassic iodide, and standard silver solution added to opalescence, the reaction will indicate sharply the total cyanogen present in the double cyanide even in presence of ferrocyanides. If to a solution of potassic zinc cyanide be added a small quantity of ferrocyanide of potassium, and the silver solution added, the flocculent precipitate of what I suppose to be normal zinc ferrocyanide (Zn_2FeCy_6) appears, the end-reaction is fairly sharp, and indicates 19.5 parts of cyanide of potassium out of the actual molecular contents of 130.2 KCy. If, however, an excess of ferrocyanide be present, the flocculent precipitate does not appear, but in its place one gets an opalescence which speedily turns to a finely granular (sometimes slimy) precipitate of potassic zinc ferrocyanide, $K_2Zn_3Fe_2Cy_{12}$. This introduces a personal equation into the analysis of such a solution, for if the silver solution be added rapidly the results are higher than if added drop by drop, as this ferrocyanide of zinc and potassium separates out slowly in dilute solutions alkaline or neutral to litmus paper.

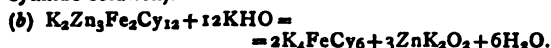
This ferrocyanide is decomposed by—

- (a) Potassic, sodic, or calcic cyanide, &c.;
- (b) Potassic or sodic hydrate;
- (c) Potassic or sodic carbonate;

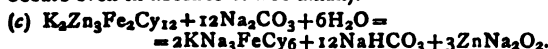
as shown by the following equations:—



(This equation is proved by mixing solutions of potassic zinc cyanide with one of potassic ferrocyanide, no precipitate occurs. Potassic zinc ferrocyanide is dissolved by cyanide solution).



(Potassic zinc ferrocyanide is readily dissolved by caustic alkali. If potassic (or sodic) zinc oxide in solution be added to potassic ferrocyanide no precipitate occurs even in absence of free alkali).



(This is similar to the (b) reaction, with the difference that carbonates are converted into bicarbonates).

I will now draw your attention to the equations involved in the reaction previously described. As the percentage of alkalinity is definite, and consists of a portion of potassic cyanide loosely combined with zinc cyanide more firmly united with less cyanide than corresponds

in carbonates and bicarbonates, by reversing the process, adding bicarbonate of soda, free from carbonate, to the solution to be titrated for hydrocyanic acid and free cyanide. This is the one instance where hydrocyanic acid turns carbonic acid out of its combinations, and as such is interesting.



I will now proceed to describe the method of analysis.

1. *Free Cyanide*.—50 c.c. of solution is taken and titrated with silver nitrate to faint opalescence or first indication of a flocculent precipitate. This will indicate (if sufficient ferrocyanide be present to form a flocculent precipitate of zinc ferrocyanide) the free cyanide, and cyanide equal to 7.9 per cent of the potassic zinc cyanide present.

2. *Hydrocyanic Acid*.—To 50 c.c. of the solution add a solution of bicarbonate of potash or soda, free from carbonate or excess of carbonic acid. Titrate as for free cyanide. Deduct the first from the second result

$$= HCy \text{ 1 c.c. } AgNO_3 = \frac{0.04145}{5} = 0.00829 \text{ p. c. HCy.}$$

3. *Double Cyanides*.—Add excess of normal soda (caustic) to 50 c.c. of solution and a few drops of a 10 per cent solution of KI, titrate to opalescence with $AgNO_3$. This gives 1, 2, and 3. Deduct 1 and 2 = K_2ZnCy_4 as KCy less 7.9 per cent.

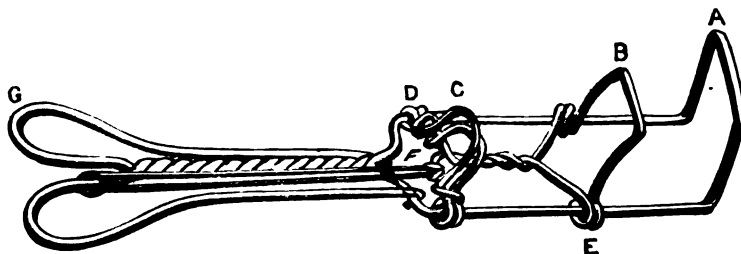
A correction is here introduced. The KCy found in 3 is calculated to K_2ZnCy_4 . Factor: KCy (as K_2ZnCy_4) $\times 0.9493 = K_2ZnCy_4$. Add to this 7.9 per cent of total, or for every 92.1 parts K_2ZnCy_4 add 7.9 parts. If this fraction, calculated back to KCy, be deducted from 1, we get the true free cyanide (calculated to KCy).

(To be continued).

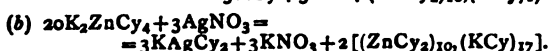
A CONVENIENT FORM OF UNIVERSAL HAND-CLAMP.

By PETER T. AUSTEN and W. A. HORTON.

THE various holders and hand-clamps used for holding test-tubes and smaller forms belong, as a rule, to two classes. The bite is effected either by a spring or by



with K_2ZnCy_4 , I venture to propose for provisional adoption the following equations representing the neutralising of K_2ZnCy_4 by acid and silver nitrate respectively:—



Here is a point for investigation, as to whether there is more than one definite crystallisable salt containing $K + Zn + Cy$, neutral to phenolphthalein, and soluble in water, or whether $ZnCy_2$ is soluble in a solution of K_2ZnCy_4 and produces neutrality to phenolphthalein.

For the estimation of free hydrocyanic acid I have made use of Siebold's ingenious method for estimating alkalis

pressure exerted by the hand. The difficulty with the first class of holders is that the spring is often inconveniently strong for delicate tubes, and not strong enough for flasks. The second class often fails when long-continued holding is involved, as muscular pressure relaxes after a time.

The following little device was worked out to afford a convenient holder that should take from nothing up to a diameter of an inch and a half, and yet allow a grasp which corresponds to the weight of the object held, and also not tire the hand, no matter how long it is held.

The clutch B slides on the parallel bars A, and is slightly smaller than the counter-clutch A. This, with its curvature, allows it to grasp any object, no matter how small, that is placed between B and A. A double bearing,

to insure ease of movement, is effected by winding the wire at D. The double arch C allows the thumb to press easily and comfortably against it, and act as a knee-joint. The swell G keeps the handle in the grasp, and the rubber strap F brings the travelling clutch back and opens the clamp as soon as the pressure is removed from C.

To use the apparatus, the handle is securely grasped and the end of the thumb is placed against C. On straightening the thumb, in the manner of a knee-joint, the object is tightly held between the clutches. The hand does not tire on continued holding, because the pressure is taken in a straight line on the bones of the thumb, and hence calls for no slight a muscular action as to be practically inappreciable.

The clamp is manufactured by Ermei and Amend.—*Journal of the American Chemical Society.*

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 21st, 1895.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Joseph Edwin Alger Blyde, Nether House, Rammoor, Sheffield; Arnold Eiloart, 2, Lansdowne Road, East Croydon; Walter Thomas Grice, 9, Dalhousie Square, Calcutta; James William Helps, 3, Tavistock Road, Croydon; Laurence W. Matthieson, 104, Grove Road, Bow, E.; Thomas Francis Rutter, The Huish School, Taunton; Arthur Philip Salt, Sunnyside, Pinner Road, Harrow; Amrita Lal Sircar, 51, Sankaritola, Calcutta; Benjamin Bernard Turner, 28, Lady Somerset Road, N.W.; and of Cass L. Kennicott, 4050, Ellis Arc, Chicago, Ill., U.S.A., approved by the Council under By-laws 1, 3.

The PRESIDENT announced that a letter of thanks had been received from the French Academy, for the Address presented by the Society on the occasion of the centenary of the Academy, on October 25th.

Of the following papers those marked * were read :—

*135. "*The Influence of Temperature on Refractive Power, and on the Refraction Equivalents of Acetylacetone and of Ortho- and Para-toluidine.*" By W. H. PERKIN, Ph.D., F.R.S.

The author points out that whilst he has proved that the refraction equivalent of certain compounds is subject to variation at different temperatures, and Brühl has observed the same fact, his numbers, and those obtained by Brühl, are not in agreement. In the case of acetylacetone, the toluidines, and other compounds, it is observed that the two sets of determinations agree closely for ordinary atmospheric temperatures, but at higher temperatures Brühl's numbers show an increase, whilst the author obtains smaller numbers at higher temperatures. The author has satisfied himself that the apparatus used by him (*Trans.*, 1892, 288) consisting of a hollow prism heated in an air-bath, furnishes uniform results, and by making observations with different specimens of material, he has proved that the differences between his numbers and Brühl's cannot be ascribed to impurity. Since the results for higher temperatures obtained by Nasini and Bernheimer, and by Kettler, using more or less independent methods, agree with the author's, he concludes that there must be some hitherto undiscovered error in the use of Brühl's refractometer at any temperature much above that of the atmosphere.

*136. "*The Evolution of Carbon Monoxide by Alkaline Pyrogallol Solution during Absorption of Oxygen.*" By FRANK CLOWES, D.Sc.

It has long been known that under certain conditions carbon monoxide is evolved during the absorption of oxygen by alkaline pyrogallol. When a solution, 100 c.c. of which contains 10 grms. of pyrogallol and 24 grms. of potassium hydroxide, is used for the absorption of oxygen, it evolves no carbon monoxide until the percentage of oxygen in the gaseous mixture exceeds 28. The carbon monoxide evolved, however, increases in amount as the percentage of oxygen rises above that limit, until the carbon monoxide finally reaches about 6 per cent of the volume of oxygen absorbed.

The process of estimation of oxygen is rendered perfectly accurate if the carbon monoxide which has been produced during the absorption is removed by means of cuprous chloride solution before the reading is taken.

Experiments with pyrogallol solution containing larger proportions of potassium hydroxide than that given above proved that the evolution of carbon monoxide may be entirely prevented under all conditions if the potassium hydroxide is present in sufficiently large proportion.

A solution, 100 c.c. of which contains 10 grms. of pyrogallol, and 120 grms. of potassium hydrate, proved perfectly satisfactory in this respect; the weight of pyrogallol may be reduced to 5 grms. in this solution.

A solution containing 18 per cent of quinol (hydroquinone) and 24 per cent of potassium hydroxide absorbed oxygen slowly, but the absorption was complete, and no carbon monoxide was evolved.

It is therefore evident that serious error may arise in estimating the proportion of oxygen present in a mixture containing only small proportions of other gases, unless the absorbent pyrogallol solution is prepared of suitable strength, or unless the absorption of oxygen is followed by the treatment of the residual gas with cuprous chloride solution.

*137. "*The Composition of the Limiting Explosive Mixtures of various Combustible Gases with Air.*" By FRANK CLOWES, D.Sc.

A series of experiments were made with mixtures in varying proportions of each combustible gas with air. A flame was brought into contact with each mixture, sometimes above and sometimes below, and it was noted whether the mixture burnt back independently of the external air. For each combustible gas there was thus obtained a lower percentage below which the mixture would not burn independently, and a higher percentage, above which the gas burnt independently only when it was supplied with more air.

The limiting percentages were as follows:—For methane, 5 and 13; for hydrogen, 5 and 72; for carbon monoxide, 13 and 75; for ethylene, 4 and 22; for water-gas, 9 and 55; for coal-gas, 5 and 28.

It was also proved that many mixtures which were outside but close to the above limits, and which could not be fired from above could be fired from below.

Hence it is inferred:—

1. That the limiting explosive mixtures for different combustible gases vary widely.
2. That methane shows the narrowest limits, hydrogen the widest limits.
3. That the risk of a mixture being fired explosively increases with the different gases in the following order:—Methane, ethylene, coal-gas, water-gas, carbon monoxide, hydrogen.
4. That the risk of explosion is greater when the mixture is kindled from below than when it is kindled from above.

DISCUSSION.

Mr. BENNETT H. BROUGH considered that it would have been a valuable addition to Professor Clowes's investigations if the action of other methods of firing had been tried. For it had to be remembered that colliery explo-

sions were sometimes due to inflammation by sparks such as were produced by picks. Some interesting experiments had recently been made in the Moravian Ostrau coalfield in Austria with an apparatus for testing the liability of gaseous mixtures to inflammation in that way. A wheel was mounted on a vertical axis inside a casing, which was hermetically sealed and provided with a large removable cover. Definite proportions of gas were introduced and mixed with the air by revolving the wheel. An iron bar sliding through the casing was brought against the revolving wheel, and in case of an explosion the cover, which was secured by a chain, was blown off without further damage.

*138. "Note on the Estimation of Butyric Acid." By W. H. WILCOX, B.Sc.

In the estimation of butyric acid in the presence of acetic and formic acids, the acids were neutralised by a known excess of calcium carbonate. Hydrochloric acid was added in sufficient amount to neutralise the free calcium carbonate and to liberate the butyric acid from the calcium salt. The solution was distilled, and when the greater part had passed over, steam was passed through the liquid as long as the distillate continued acid. The distillate, which contained the butyric acid, was boiled with pure barium carbonate, the solution filtered, and evaporated to dryness.

It was found that when dried at 100° C., the salt did not attain a constant weight even after it had been heated for several weeks, diminutions of about 2 m.grms. (with 1 to 2 grms. of salt) occurring after heat had been applied for three hours. This loss of weight did not occur at and below 80°.

Some barium butyrate was prepared, and was found to lose weight in a similar manner. At 90–100° C. losses of about 2 m.grms. occurred with three hours heating of 1.5 grms. of salt, and even at 85° C. loss of weight occurred on continued heating. When the salt was kept at 80° C., however, it speedily arrived at a constant weight, which was not altered by continued heating.

These results show that in the estimation of mixtures of the volatile fatty acids, when butyric acid is present, the fraction of salts containing the butyrate must be dried at a temperature not exceeding 80° C.; if this temperature is exceeded, loss of weight occurs owing to the decomposition of the butyrate.

139. "Some Derivatives of Anthraquinone." By EDWARD SCHUNCK, Ph.D., F.R.S., and LEON MARCHLEWSKI, Ph.D.

The authors have prepared the three hitherto unknown methyl purpuroxanthins. One of them was obtained by condensation of *o*-toluic acid with *m*-hydroxybenzoic acid. It crystallises in orange-coloured needles (m. p. 246°). Its diacetyl derivative is nearly colourless (m. p. 195°).

The other two methylpurpuroxanthins were obtained by condensation of *m*-toluic acid and *m*-hydroxybenzoic acid. The mixture of methylpurpuroxanthins produced, yielded two distinct compounds by fractional crystallisation from a mixture of alcohol and benzene. The constitution of these compounds was determined by studying the products of their oxidation. The more soluble one gave, on treatment with nitric acid, trimellitic acid, while the other one gave, on similar treatment, hemimellitic acid.

The authors point out that the constitutional formulæ proposed by them (*Trans.*, 1894, 186) for the ethers of alizarin are supported by the work of Lagodzinski (*Ber.*, 1895, 1427), who obtained a monomethyl ether of alizarin by the condensation of hemipinic acid with benzoic acid.

The authors give a more precise account of the ethers of anthraquinoneoxime, mentioned by them in a preliminary paper previously published (*Ber.*, 1894, 2125). The methyl ether melts at 147°, the ethyl ether at 97°, and the benzyl ether at 82°.

140. "Efflorescence of Double Ferrous Aluminium Sulphate on Bricks exposed to Sulphur Dioxide." By DAVID PATERSON.

The author has analysed the efflorescence which appears on bricks composing chambers in which wool is bleached with sulphur dioxide. Four analyses were made, and the results agree well with the percentages required by the formula $\text{Al}_2(\text{SO}_4)_3 \cdot \text{FeSO}_4 \cdot 24\text{H}_2\text{O}$. The salt forms white fibrous crystalline masses resembling asbestos in appearance. It is evidently identical with the salt often found in volcanic regions, and the author's analyses agree well with those made by Forchhammer of a specimen obtained from Iceland.

Collective Index of the Transactions, Abstracts, and Proceedings of the Chemical Society.

Volume II., 1873 to 1882. Volume III., 1883 to 1892.

The Council, having determined to publish a Collective Index of their publications from 1873 to 1892 inclusive, will issue copies to Fellows who may notify their wish to receive them. Both volumes will be sent to those who were Fellows of the Society before the end of 1882. Volume III. will be sent to Fellows who have joined the Society between 1st January, 1883, and 31st December, 1892. Fellows who are ineligible to receive copies *gratis*, and those who may have neglected to apply for them within the prescribed period, may obtain them by purchase at a price to be hereafter fixed. Fellows who desire the Index should notify their wish by letter, enclosing 1/- for cost of distribution, &c., to the Assistant-Secretary, Mr. Robert Steele, Chemical Society, Burlington House, W., before 31st December, 1895. For Fellows resident abroad, who should remit 2/-, which may be paid with their annual contribution, the time will be extended to March 1st, 1896.

A few copies of Vol. I. (1841–72) can still be obtained, price 3/- post free.

Research Fund.

A meeting of the Research Fund Committee will be held in December.

IMPERIAL ACADEMY OF SCIENCES OF VIENNA.

Session of the Mathematical and Natural Science Section, of October 24th, 1895.

"On the Red Spectrum of Argon." By Dr. J. M. EDER and Dr. E. VALENTA.

By the kindness of Lord Rayleigh we obtained a specimen of argon gas which had been carefully introduced into vacuum tubes by Herr Goetze, of Leipzig. The pressure in the tubes which we used in our experiments was from 1 to 3 m.m. For the spectroscopic analysis of the argon we used a concave grating having a radius of curvature of $\frac{1}{2}$ metre, employing the photographic method. We examined the red and the blue spectrum obtained by working according to the directions of Mr. Crookes, with weak sparks without Leyden jars, or with sparks from the jars.

For the red spectrum of argon we obtained the numbers quoted below. The lines marked with asterisks in the author's tables are present also in the blue spectrum of argon. The other lines are peculiar to the red argon spectrum. The especially characteristic lines of the red argon spectrum are:— λ 4628.56, 4596.22, 4522.49, 4510.85, 4300.18, 4272.27, 4259.42, 4251.25; especially the group 4200.76, 4198.42, 4198.07, 4164.36, 4158.63; and further, 4044.56, 3949.13, 3834.83. Further measurements will appear in the *Transactions of the Imperial Academy*. It must also be remarked that the red argon spectrum is well resolved when the double line $\begin{cases} 4191.15 \\ 4190.75 \end{cases}$ appears clearly separated.

If the blue and the red argon spectrum belong to two elements, which is by no means improbable, the above lines would be the main characteristic lines of one of them.

NOTICES OF BOOKS.

A Handbook of Industrial Organic Chemistry: adapted for the Use of Manufacturers, Chemists, and all interested in the Application of Organic Materials in the Industrial Arts. By SAMUEL P. SADTLER, Ph.D., F.C.S., Professor of Chemistry in the Philadelphia College of Pharmacy, and in the Franklin Institute of the State of Pennsylvania, &c. Second and Revised Edition. 8vo., pp. 537. Philadelphia: J. B. Lippincott Company. London: 10, Henrietta Street, Covent Garden. 1895.

PROF. SADTLER admits that there is, on the one hand, no lack of technological manuals for separate chemical industries, such, e.g., as tanning and dyeing; and, on the other hand, of encyclopædic works embracing the entire compass of the chemical arts, but that there is a scarcity of works which attempt to give, within the compass of a single volume, a general view of the various industries based upon the applications of chemistry to the arts." The reason of this rarity is not difficult to find. The chemical industries are now so numerous and so elaborate that to give in a single volume anything beyond a mere sketch of each, of comparatively little practical value, is indeed an arduous task. To escape this difficulty the author confines himself in the volume before us to the organic arts, and promises to give an account of the inorganic chemical industries in a future volume. This expedient certainly reduces the bulk of the matter to be dealt with, but it encounters the difficulty that there is no hard and fast boundary line between the organic and inorganic chemical arts.

If we turn to the subjects discussed in this volume—such as tanning, soap-making, dyeing, bleaching, and tissue-printing—we find that they are at once organic and inorganic. The same must be said of the manufacture of chemical manures, of painters' colours, and writing inks, which are not mentioned in the work before us, and each of which would likewise overstride the boundary line. Again, when the companion volume appears the work will no longer give a view of the chemical industries within the bounds of a single volume.

If we might suggest, a principle of division preferable to that of "organic and inorganic" might be found, though it would not be easy to find scientific names for the two respective groups of industries. Let us suppose, by way of explanation, that on visiting some strange town we were to enquire what chemical works there were in the district. We should then feel startled if we were told of a number of dairies, bake-houses, breweries, and sugar-works. Yet the processes carried on in these establishments are unquestionably chemical. Still we feel, however difficult it may be to put the distinction in words, that they do not belong in the same category as bleach-works, soap-works, or tanneries.

Passing from questions of arrangement to the subject-matter itself, we must congratulate Dr. Sadtler on the rare felicity with which he has condensed into so small a space so large an amount of valuable matter. Oversights and errors are indeed rare. We note merely a passage which seems to convey the impression that indigo is always applied to textile goods by means of the cold vat, whilst in fact the warm vats are chiefly used in woollen-dyeing.

A most valuable feature of this book is the biographical department subjoined to each section. The student is thus furnished with a master-key which opens to him all the details of technical chemistry.

Hints on the Teaching of Elementary Chemistry in Schools and Science Classes. By W. A. TILDEN, D.Sc., F.R.S. Crown 8vo., pp. 76. London and New York: Longmans, Green, and Co. 1895.

MANUALS of elementary chemistry are far from rare,—too plentiful, indeed, as we are sometimes tempted to think. But the little work before us is exceptional in its character. It is addressed not to students, but to teachers, and thoroughly good lessons does it convey. Pity, though, we must add with bated breath, that any teacher of chemistry, or of any science, should need such hints.

In the first sentence of the Preface Dr. Tilden rejoices over the issue of a new "Syllabus." It may be a very important advance in the teaching of chemistry, as giving more scope to the discretion of the teacher. But there would be still greater room for congratulation if the new "Syllabus" were the last of the race! It is appropriately urged that the teacher should devote some part of his time to extending and consolidating his own knowledge. Should he need any such reminder? We find a denunciation of the "crammer," but due reflection will tell us that this unlovely being is a by-product of examinationism.

We are inclined to agree with Prof. Tilden when he expresses the opinion that the study of chemistry, when rightly taught, is the best means of cultivating the faculty of observation. The general incapacity of distinguishing objects unless they differ markedly in size or colour is duly regretted. This incapacity is, we fear, most striking in those who have "enjoyed" a classical education.

The author points out that chemistry cannot be learnt by reading alone. The eye and the hand must first be trained. One of the dangers of working from text-books is that "the student imbibes the idea that the subject is complete, rounded off, and finished, and that he sees no room for further inquiry."

It will not, we hope, be deemed irrelevant if we point out the fatal blow which the examination system has just received. In the Chinese Empire, for ages, all statesmen, generals, judges, and magistrates have been selected by competitive examination. The outcome has been the collapse which the world has just witnessed. Intellectually and morally the examinee has been weighed in the balance and found utterly wanting.

Simple Methods for Detecting Food Adulteration. By JOHN A. BOWER. With 36 Illustrations. Published under the Direction of the General Literature and Education Committee. Small post 8vo., pp. 118. London: Society for Promoting Christian Knowledge. 1895.

TIME was when the publications of the Society for Promoting Christian Knowledge were spoken of with scanty respect, but the number of valuable works by writers of acknowledged merit which have appeared with the imprimatur of the Society have done away with such an unjustifiable feeling. Mr. Bower's work is not intended as a guide for the student or a work of reference for the professional analyst, but it is calculated to guard the general public against frauds which affect their pocket, if not their health.

The author concludes that "adulteration is decidedly on the decrease," and again, that "our food is not adulterated to an alarming extent." Yet he qualifies these disclaimers by the admission that, as recently as the year 1891, "about 12 per cent of all the food sold in this country was adulterated," that coffee is sometimes sophisticated "to the amount of 75 per cent," that milk may contain from 20 to 30 per cent of added water. Now these facts show, we submit, that adulteration is still carried on to an "alarming extent," and that the apathy of the public—the persons thus defrauded—is in itself almost criminal.

Mr. Bower quotes several clauses of the "Sale of Food and Drugs Act," which has many deficiencies. Thus, in the case of coffee, to sell mixtures of coffee and chicory not conspicuously labelled as such is undoubtedly punishable; but if an enterprising tradesman wishes to sell chicory at the price of coffee, and of course to people who prefer coffee and do not want chicory, he needs merely sell his mixture as "French coffee," or "Coffee as in France," and he escapes the provisions of the Act! It would be easy to put a stop to this disgraceful fraud. Until lately it was practicable to avoid this fraud by always buying coffee unground; but criminal ingenuity now manufactures spurious coffee-beans, as well as spurious peppercorns, nutmegs, and, we believe, gall-nuts. Such devices require a punishment heavier than fines. It should be enacted that any person designing, constructing, vending, offering for sale, or using any machine, mould, stamp, or die for making up any powder, paste, or pulp into the shape of any berry, nut, or seed used in food or medicine, or selling any products thus moulded, shall on conviction be sentenced to imprisonment for not less than six months.

A fraud in the sugar-trade has escaped the author's notice. Continental growers of beet-sugars colour some of their unrefined product with yellow coal-tar dyes, and export the precious mess to England under the name of Demerara sugar! Thus they kill two birds with one stone. They sell their rank-tasting produce for more than it is fairly worth, and they damage the reputation of genuine Demerara sugars. Even the bees and the wasps know the difference between beet- and cane-sugars, and reject the former if the latter is accessible.

We believe that this work, addressed as it is to the general public, will aid in the necessary task of creating a healthy hostility to sophistication and sophisticators.

An Exercise Book of Elementary Practical Physics. By RICHARD A. GREGORY, F.R.A.S. (Oxford University Extension Lecturer). Pp. 172. London and New York: Macmillan and Co. 1895.

THIS book, we are told on the title-page, is intended for "organised Science schools under the Department of Science and Art, evening continuation-schools and elementary day-schools." We further learn that it has been "arranged according to the Head-masters' Association Syllabus of Practical Physics." The table of contents reproduces the Head-masters' Association Syllabus, with a few changes and additions.

The reader will perhaps find the term "physics" here used in a sense which he scarcely expected.

Light, electricity, and magnetism are not touched upon at all, and but very slightly. The main subject of the work is mechanics, with meteorology. What the book undertakes to teach, however, is well taught, and those who have made use of it, whether teachers or students, will not find that they have anything to unteach or unlearn.

Franklin Institute: Announcement and Programme of Lectures, 1895-1896. No. 15, South Seventh Street, Philadelphia.

THE organisation of this Society is rather complex. It has a board of trustees; a staff of officers and managers; a board of management; two curators; four professors for the respective departments of mechanics, physics, chemistry, and economic geology; and a number of committees. There are five classes of members, viz., contributing members, stockholders, life members, permanent members, and non-resident members.

Among the lectures in the ensuing session the following are, from our point of view, the most interesting:—"Metallurgical and other Features of Japanese Swords," by Mr. B. S. Lyman; "Recent Improvements in the Chemical Treatment of Fibres and Fabrics," by L. J. Matos; "Modern Theories of Fermentation," by Dr. F.

Wyatt; "Electro-metallurgy of Aluminium," by Dr. J. W. Richards; "Some Recent Work in Molecular Physics," by Prof. R. A. Fessenden; "What constitutes a Good and Safe Drinking Water?" by T. M. Drown, M.D., LL.D., of Lehigh University.

Craft Instruction: Photography and Process.

THIS pamphlet, which is issued at the Polytechnic Institution, W., bears no author's name. It consists of an elaborate prospectus of the photographic department of the Polytechnic Institution, which is now in its fourteenth session. There are also the advertisements of a number of manufacturers of, and dealers in, cameras, lenses for photography, and accessory appliances.

CORRESPONDENCE.

ON THE

PLACE OF HELIUM IN THE CLASSIFICATION OF ELEMENTARY SUBSTANCES.

To the Editor of the Chemical News.

SIR,—In the report of the recent meeting of the Physical Society of November 22nd in the CHEMICAL NEWS (vol. lxxii., p. 266), in which the investigations of Profs. Runge and Paschen on the spectrum of the new gases from clèveite are referred to, I observe that Dr. Gladstone places these gases between hydrogen and lithium, in order that they may come into a classification based on a supposed periodicity of chemical properties when the elements are arranged in seriatim order of their atomic weights. I have shown elsewhere why the new gases cannot be allocated to the places assigned to them by Dr. Gladstone, and have to express my surprise that this chemist should, by loose arithmetic and still looser assertions, endeavour to controvert the reasons I have given for placing the new gases at the head of the second and third series of my table of elementary substances. The mis-statements to which I take exception as hindering the progress of chemical science are—

(1). That the successive differences between the atomic weights of adjacent members of the metals in the first group in Mendeleeff's table showed that these differences increased as we go downward.

And (2). "That if the new gases have atomic weights of, say, 2 and 4, we should have for these differences 2, 2, 3, 16, 16, 26, &c., instead of 6, 16, 16, &c., as at present."

Now the incorrecness of these alleged increasing differences in the atomic weights will be at once apparent from a simple inspection of the first group in Mendeleeff's table, in which I have included Dr. Gladstone's numbers for the new gases.

	Diff.
H = 1	
HI ₁ = 2	- 1
HI ₂ = 4	- 2
Li = 7	- 3
Na = 23	- 16
K = 39	- 16
Cu = 63	- 24
Rb = 85	- 22
Ag = 108	- 23
Cs = 133	- 25

It will, moreover, be evident that, even if the successive differences between the atomic weights in the first group increased as Dr. Gladstone alleges, the numerical relation would afford no ground for placing the new gases above lithium, as they might for the same reason be placed above the typical members of any other group in Mendeleeff's table.

In my paper on "Some New Relations of the Atomic Weights" published in the *CHEMICAL NEWS* (vol. xxxviii., p. 66, &c.), I have shown that in the first group or series H_n all the atomic weights after Na have a constant difference of 23; and in the second series H_{2n} a common difference, after Mg, of 24. As these series are of considerable interest at the present time, I will, by your permission, reproduce the part of my table containing them, with the addition of the accepted atomic weights for the purpose of comparison.

1.	+ H_n -		+ H_{2n} -	
2.	Li = 7		Gl = 8	
	 7*		 9 ²	
3.	Na = 23	F = 19	Mg = 24	O = 16
	 23	 19	 24	 16
4.	K = 39	Cl = 35	Ca = 40	S = 32
	 39	 35 ⁵	 40	 32
5.	Cu = 62		Zn = 64	
	 63 ³		 65	
6.	Rb = 85	Br = 81	Sr = 88	Se = 80
	 85	 80	 87 ⁵	 79
7.	Ag = 108		Cd = 112	
	 108		 112	
8.	Cs = 131	I = 127	Ba = 136	Te = 128
	 132	 127	 137	 128
9.	$x = 154$		$x = 160$	
10.	$x = 177$		$x = 184$	
11.	Hg = 200		Po = 208	
	 200		 207	

* Accepted atomic weights.

In this table it will also be seen that the negative elements of the first and second series after Cl and S have constant differences of 46 and 48 respectively, or double the differences of the atomic weights of the members of each adjoining positive series of elements. The common difference of 16 of the atomic weights in the table above K, Cl, Ca, and S are equally interesting and significant. I have already, in the paper referred to, directed attention to the common difference of 4 between the halogens and the alkaline metals in homologous positions, and the common difference of 8 between the oxygen series and the alkaline-earth metals in similar positions: while the fact that the theoretic atomic weights of the members of the four series, when taken together, differ by less than half of one per cent from the actual determinations establishes the law of the multiple relations and constant differences of the atomic weights of these series on a solid and immutable basis—the heritage of chemical science for all time.—I am, &c.,

HENRY WILDE.

December 3, 1895.

CHEMICAL EDUCATION.

To the Editor of the *Chemical News*.

SIR,—Your correspondent "W. A. D." has certainly pointed out one of the causes why chemical research is not more abundant in Britain, and why many of our chemical arts are declining. The evil factor is the exorbitant price of alcohol, a reagent constantly required both in research and in manufactures as far as organic products are concerned. Methylated spirit did, indeed, to a great

extent lighten the burdens of the chemist, but, *suadente diavolo*, this concession has now been stultified by the excise ukase demanding the further addition of mineral naphtha. Whether this stipulation has been made in the fancied interest of the revenue or of "temperance" it has been decided without any regard to the interests of Science or Industry. If it is necessary to render methylated spirit absolutely undrinkable the addition of a mere trace of Dippel's animal oil, as the German Government allows for alcohol to be used in the colour industries, would have met the difficulty.

It is perfectly true that a methylated spirit may be obtained free from mineral naphtha, by dint of a sufficient unrolling of red tape, and with the pleasant condition of rendering our laboratories or works open to the visits of the exciseman. The only marvel is not that the Government took a foolish step, but that the interests threatened did not at once rise on the defensive and insist on the withdrawal of the oppressive regulation.—I am, &c.,

W. S.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxi., No. 21, November 18, 1895.

On an Element, probably Novel, existing in the Terbias.—Lecoq de Boisbaudran.—I solicit the Academy for permission to submit a paper which I have written formerly (May 3, 1886) on an absorption-band observed in certain portions of a fractionation of terbia, and which I believe to be characteristic of a peculiar element. I had hoped to continue the study of this band, but having successively used up my samples of terbia in various experiments, there remains so little of this earth that further fractionations have become impossible. My memorandum of 1886 is:—My present terbia is an earth of a deep reddish brown, the hydrochloric solution of which gives only a weak absorption spectrum, entirely composed of the bands of dysprosium, and of a band which appears to belong to a new element. This is a brief description of this band:—Micrometer, 140.8; λ , 487.7. Observations: Apparent medium of a nebulous band, a little more indistinct on the left than on the right. Breadth, from 2 to 2½ degrees of the micrometer; intensity, moderate. The band 140.8 does not appear to belong to Ta_2O_5 , since it is seen at least as strongly in earth of a little brighter colouration, as in my purest terbia. It does certainly not belong to dysprosium, being more or less strong than the band $Dy \beta$ 148.3, according to the products examined. Provisionally I shall name the earth producing the band 140.8 ($\lambda=487.7$) Z δ .

Origin of Atmospheric Oxygen.—Dr. T. L. Phipson. The author's views on this subject have already appeared in the *CHEMICAL NEWS* for the years 1893 and 1894.

Synthesis of Methyleugenol. Constitution of Eugenol.—Ch. Moureu.—The author causes allyl iodide, $ICH_2-CH=CH_2$, to react upon veratrol in presence of zinc powder. The method admits of generalisation, and he intends to apply it to the synthesis of safrol, anethol, and estragol.

Cholesterines of the Cryptogams.—E. Gérard.—The cholesterines existing in the lower plants all belong to the group of ergosterine.

Distribution of Pectase in the Vegetable Kingdom, and on the Preparation of this Diastase.—G. Bertrand and A. Malleuvre.—Pectase may be considered as occurring universally in green plants. It is especially abun-

dant in the leaves, from which it is extended into the other organs. The richness of certain leaves in pectase allows us to realise for the first time the proportion of this ferment.

Retting of Flax, and on its Microbian Agent.—S. Winogradsky.—The organism in question is relatively large, forming spores in the terminal swellings (tadpole shape). Its joints are from $10\ \mu$ to $15\ \mu$ in length by $0.8\ \mu$ in thickness. The retting of flax may be considered as a pectic fermentation in the microbiological sense of the word.

Zeitschrift für Anorganische Chemie,
Vol. viii., Parts 4 and 5.

The late Professor G. Krüss.—A faithful record of the life and activity of the late founder and editor of the *Zeitschrift für Anorganische Chemie*, with a bibliography of his memoirs and publications, truly wonderful considering his early death.

Revision of the Atomic Weight of Strontium.—Th. W. Richards.—Already inserted.

Determination of Carbon in Iron.—F. Foerster.—Among the procedures which give trustworthy values for the determination of carbon in iron, the copper-ammonium chloride can be executed with the simplest appliances at hand in every laboratory, and does not make such demands on the experience of the analyst as does, e.g., the chlorine process. Sometimes its general applicability is interfered with by the fact that some sorts of wrought irons, especially tungsten-steels if in contact with a quite neutral solution of copper-ammonium chloride, give a violent escape of gaseous hydrocarbons. In such cases the author, instead of a solution of copper-ammonium chloride, uses a solution of copper-ammonium oxalate. This is obtained by mixing a 10 per cent solution of copper sulphate with a solution of ammonium oxalate saturated in heat until the initial precipitate is re-dissolved. Of this solution, 250 c.c. are poured upon 2 to 3 grms. of the tungsten-steel to be analysed, and heated together in the water-bath at 80° for five hours. Copper separates out, and the liquid takes a green colour. It is decanted away from the residue, the copper is dissolved away with a solution of copper-ammonium chloride, when the residual carbonaceous substance, after filtration and drying, is burnt in a current of oxygen.

Atomic Weights of Nickel and Cobalt.—Clemens Winkler.—Already inserted.

Acidimetric Determination of Molybdic Acid.—Karl Seubert and W. Pollard.—In the summer of 1890, by occasion of the analysis of a hydrated molybdic acid which had crystallised out of a molybdenum solution, we made the experiment of determining the proportion of free acid in the precipitate by supersaturation with soda-lye and titrating back with hydrochloric acid, using phenolphthalein as indicator. The results were satisfactory. Various indicators were used, but only phenolphthalein and litmus proved satisfactory. The lye must be carefully prepared, and should be preserved from carbonic acid.

Quantitative Separation of Metals by Hydrogen Peroxide in Alkaline Solutions.—P. Jannasch and A. Röttgen.

Action of Heat upon Carbon Sulphide.—Henryk Arctowski.—By the action of heat upon the vapour of carbon sulphide, the author obtains the substance which occasions the unpleasant odour of carbon disulphide. It is probably the same as Bela v. Langyel's carbon sesquisulphide.

New Nitroso-compounds of Iron.—K. A. Hofmann and O. F. Wiede.—The authors have succeeded in obtaining well-characterised salts of an acid of the formula $\text{Fe}(\text{NO})_2\text{SSO}_2\text{OH}$.

Cause of Osmotic Pressure and of Ionisation (Electrolytic Dissociation).—J. Traube.—A continuation of a very extensive memoir, not suitable for abstraction.

Determinations of the Molecular Weights of Solids, Liquids, and Solutions.—J. Traube.—Not capable of useful abridgment.

Action of Dry Hydrogen Chloride upon Serpentine.—R. Brauns.—This paper is chiefly a critique of the researches of Clarke and Schneider. It is concluded that the hydrochloric gas employed by those chemists was mixed with traces of water, and hence could not be regarded as sufficiently dry. It was rendered capable of reaction by the presence of watery vapour, and has thus occasioned the decomposition of the magnesium silicate. Water was formed by the decomposition of these silicates, and promoted further decomposition. It cannot be concluded from the occurrence of the reaction in hydrogenous minerals in what manner their hydrogen is combined. The number of the $\text{Mg}-\text{OH}$ groups cannot be inferred from the quantity of the chlorides formed. Hence the experiments of Clarke and Schneider—in as far as they refer to the action of hydrogen chloride upon silicates—are not adapted to yield a decision on the constitution of the silicates examined.

Simple Method of General Applicability for the Determination of Water in Silicates.—P. Jannasch and P. Weingarten.—This paper requires the accompanying figure.

The Chemical Composition and Constitution of Vesuvian.—P. Jannasch and P. Weingarten.—A tabular view of the analytical composition of vesuvian from various localities, distinguishing the specimens containing fluorine and those from that halogen.

Opening Up Silicates by the use of Pure Lead Carbonate.—P. Jannasch.

Crystalline Copper Ferrocyanides.—J. Messar.—A full account of the formation, composition, and properties of sodium cuproferrocyanide, sodium cuprocyanide, potassium cuproferrocyanide, ammonium cuproferrocyanide, ammonium cupriferricyanide, magnesium cuproferrocyanide, magnesium cupriferricyanide, calcium cupriferricyanide, strontium cupriferricyanide, barium cupriferricyanide, and ferrocyanocuprammonium.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xxxi., No. 3.

This issue contains no chemical matter.

MISCELLANEOUS.

Salters' Company's Research Fellowship.—The Executive Committee of the City and Guilds of London Institute are inviting applications for the appointment to the Salters' Company's Research Fellowship for the ensuing year. The Fellowship was founded by the Salters' Company for the encouragement of higher research in chemistry in its relation to manufactures, and particulars of the scheme under which the award is made may be had on application to the Honorary Secretary, at the Head Office of the Institute, Gresham College, Basinghall Street, E.C. The results of the researches by Dr. Martin O. Forster, the Salters' Research Fellow for the current year, at the Institute's Central Technical College, were communicated to the Chemical Society at its last meeting.

Mercury-thymolo-acetate.—E. Merck.—The CHEMICAL NEWS not being a medical organ, we cannot give instruction for the use of any medicine, especially one of the "proprietary" class. The only point we can notice is that the bacillus of tuberculosis is very similar to that of syphilis.

MEETINGS FOR THE WEEK.

- MONDAY, 19th.**—Society of Arts, 8. "Mechanical Road Carriages," by H. Worby Beaumont, M. Inst.C.E. (Cantor Lectures).
- TUESDAY, 17th.**—Institute of Civil Engineers, 8.
Pathological, 8.30.
Photographic, 8.
Society of Arts, 4.30. "Jamaica in the Past and Present," by Frank Cundall.
- WEDNESDAY, 18th.**—Society of Arts, 8. "Machines for Composing Letter-press Printing Surfaces," by John Southward.
British Astronomical, 5.
Meteorological, 7.30.
Geological, 8.
Microscopical, 8.
- THURSDAY, 19th.**—Chemical, 8. "Liquefaction of Air" and "Properties of Liquid Air," by Prof. Dewar, F.R.S.
Discussion on "The Constitution of Terpenes and Camphor." "Derivatives of Dimethylaniline," by Miss Evans, B.Sc.
- FRIDAY, 20th.**—Quekett Club, 8.

TO CORRESPONDENTS.

C. E. B.—It is doubtful whether the propounder of the question whether F should rank along with Cl, Br, and I could give a strictly scientific answer. He asks why it is not "usually included in that group?" He does not say "naturally" or "legitimately." Fluorine was till very lately an element of unknown properties, and hence it was commonly excluded from the group of the halogens. Its chief difference is that its oxide has not yet been obtained.

JUST PUBLISHED.

446 pages and 104 Illustrations. Price 12s. 6d.

A TREATISE ON THE MANUFACTURE OF SOAP AND CANDLES, LUBRICANTS, AND GLYCERIN.

By WM. LANT CARPENTER, B.Sc.

Second Edition, Revised and Enlarged by HENRY LEASK.

CONTENTS.

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Raw Materials: Their Sources and Preparation.
Raw Materials: Refining, Clarifying, and Bleaching.
Raw Materials: Their Proximate Analysis.
Caustic Alkali and other Mineral Salts.
Manufacture of Household Soaps: The Process of Saponification.
Treatment of Soap after its Removal from the Soap Copper: Cooling, Cutting, Drying, Moulding.
Soap—Filling and Sophisticating.
Special Soaps: Household, Laundry, Floating, Disinfectant, Hard-water, Sand, Cold-water, Powders, Manufacturers', Toilet, Transparent, Fancy, Solidified, Glycerin, &c.
Theory of the Action of Soap—Its Valuation and Analysis—Distribution and Position of the Trade.
Lubricating Oils, Railway and Waggon Grease, &c.
Candles—Raw Materials, their Sources and Preliminary Treatment.
Processes for the Conversion of Neutral Fats into Fatty Acids—The Manufacture of Commercial Stearin.
The Manufacture of Candles and Night-lights—Their Value as Illuminants. Glycerin. Bibliography. Index.

E. & F. N. SPON, 125, Strand, London.

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SALTERS' COMPANY'S RESEARCH FELLOWSHIPS.

The Court of the Salters' Company having placed at the disposal of the City and Guilds of London Institute a Grant of £150 a Year for founding one or more Fellowships for the encouragement of Higher Research in Chemistry in its relations to Manufactures, the Executive Committee of the Institute are prepared to receive applications from candidates for appointment.

Candidates must be British-born subjects. Preference will be given to students of the Institute who have completed a full Three Years' Course of Instruction in the Chemical Department of the Central Technical College, but other candidates duly qualified in the Methods of Chemical Research in its relation to Manufactures are also eligible, without restriction as to age or place of previous study. A Copy of the Scheme, giving particulars of tenure, &c., under which the Fellowships will be awarded, may be had on application at the Head Office of the Institute, Gresham College, Basinghall Street, London, E.C.

JOHN WATNEY, Honorary Secretary.

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To be Exposed, within the Faculty Hall, St. George's Place, Glasgow, on Friday, 20th December 1895, at 12 o'clock Noon, —
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PATENTS, DESIGNS, AND TRADE MARKS ACTS, 1883 TO 1888.

NOTICE IS HEREBY GIVEN that HEINRICH BAUM, of No. 28, Forsthausstrasse, Frankfurt-on-the-Main, in the Empire of Germany, has applied for leave to amend the Specification of the Letters Patent No. 12942 of 1893, for "Improvements in the Manufacture of Ortho-halogen-phenol, and in the Production of Pyrocatechine therefrom."

Particulars of the proposed Amendments were set forth in the Illustrated Official Journal (Patents) issued on the 4th December, 1895.

Any person or persons may give notice of opposition to the Amendment (on Form G), at the Patent Office, 25, Southampton Buildings, London, W.C., within one calendar month from the date of the said Journal.

(Signed) H. READER LACK,
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THE CHEMICAL NEWS.

VOL. LXXII., No. 1882.

EXAMINATION OF GASES FROM CERTAIN MINERAL WATERS.*

By ALEXANDER KELLAS, B.Sc., and
WILLIAM RAMSAY, Ph.D., F.R.S.

A SAMPLE of gas of an inflammable nature, sent to Mr. Crookes by Mr. C. Lowthian Bell, of Middlesbrough, from "Allhusen's Well," was sent on to us to be tested for argon. The usual constituents, nitrogen, hydrocarbons, &c., were removed by the usual absorbents, magnesium, copper oxide, &c., and finally by sparking with oxygen over caustic soda. The only noticeable feature was the great difficulty in removing the hydrocarbon, which for long resisted the action of red-hot copper oxide. The circulation had to be continued for two days before absorption was nearly complete. In one case (Kellas) 555 c.c. of gas gave 2 c.c. of residue, and in another (Ramsay) 950 c.c. gave 4.5 c.c. This corresponds to about 0.4 per cent of indifferent gas. The first portion was unfortunately lost, but the spectrum of the second portion was carefully compared with that of argon, and the lines were all found to be coincident. No new lines appeared, nor was any helium yellow visible.

An incombustible gas from another well at the same place was also tested, and was found to contain 0.5 per cent of argon (Kellas).

Some gas from a boiling spring near Reykjavik, Iceland, was collected last autumn (Ramsay), and, on removing the combinable constituents, 7.45 c.c. were obtained from 660 c.c. of the gas. This is a greater proportion of argon than is present in air, being 1.14 per cent. No helium could be detected in the gas, nor were there any lines which could not be recognised as belonging to argon.

It has been thought worth while to place on record these experiments, although they show nothing remarkable. We have to express our indebtedness to Mr. Noel Heaton for help kindly rendered.

THE EXPANSION OF ARGON AND OF HELIUM AS COMPARED WITH THAT OF AIR AND HYDROGEN.*

By J. P. KUERNEN, Ph.D.,
Professor of Physics in University College, Dundee, and
W. W. RANDALL, Ph.D.,
Lecturer in Johns Hopkins University, Baltimore, U.S.A.

ACCURATE comparisons of temperatures, as read with the aid of thermometers filled with different gases, have not often been made. The history of the subject may be said to have begun with the classical researches of Regnault ("Relations des Expériences," &c., 1847-62). Of recent work of this kind, that of Chappuis (*Archives de Genève* [3], vol. xx., pp. 5-36, 153-179, 248-262; also *Traité et Mémoires du Bureau International*, vol. vi.) were performed entirely at temperatures below 100°, the gases employed being hydrogen, nitrogen, and carbon dioxide. The experiments of Grunmach and Pernet (*Mémoires de la Société de Physique*, No. 3) were also conducted at temperatures below 100°. Crafts (*Comptes Rendus*, vol. xcv., pp. 836-839), has compared the readings of a number of mercury thermometers with those obtained by Regnault and by himself with a hydrogen thermometer. Wiebe and Böttcher

(*Zeitschrift für Instrumentenkunde*, vol. x., pp. 16 and 233) have determined the boiling-points of a number of liquids in terms of the expansion of air.

In connexion with the work on argon and helium in progress at University College, it was suggested by Prof. Ramsay that a comparison should be made between the readings shown by thermometers containing respectively argon, helium, hydrogen, and air. The temperatures used were:—the melting-point of ice and the boiling-points of water, chlorobenzene, aniline, quinoline, and bromonaphthalene respectively. The gas to be experimented upon was contained in a bulb about 12 c.m. long and 2.2 c.m. wide, sealed at one end to a fine capillary tube about 12 c.m. long; this, in turn, was connected with a piece of thick-walled glass tubing, having an inside diameter of about 0.2 c.m. The wider tube was fitted with a stopcock, for convenience in filling the bulb, and at its lower end was connected with a stout rubber tube, which led to a movable mercury reservoir. Near the point at which the fine capillary tube was sealed to the wider tube, a mark was made on the latter: the mercury was always brought up to this mark in the experiments, and the difference of level in the tube and in the mercury reservoir was read off, with the aid of a telescope, from a glass scale graduated in millimetres, which stood directly behind the apparatus.

The bulb of the gas thermometer was heated in one of Ramsay and Young's vapour-jackets, the mark on the stem being just below the cork closing the bottom of the jacket: consequently a small portion of the stem was not heated to the temperature of the vapour in the jacket. The error thus introduced was taken into account. No part of the mercury column which compressed the gas in the bulb was heated more than a few degrees above the temperature of the room, screens being employed to cut off radiation: the temperature of the mercury was, however, always determined as accurately as circumstances would permit, and the readings reduced to 0°. In order to protect the thermometer bulb from the effects of radiation, the jacket was shielded by an outer cylinder of thick pasteboard, with an air space between.

Since the mercury was always brought to the same point on the stem of the thermometer bulb, the volume of the gas, except for the change produced by the expansion of the glass, was in all the experiments the same, while the pressure was, of course, different for each temperature employed. For convenience the bulb was filled, in the case of each gas, at from two-thirds to three-fourths atmospheric pressure: under these circumstances the bulb was never subjected to an internal pressure greater than about 1½ atmos.

Corrections.—All pressures were reduced to 0°. The coefficient of expansion of the glass of the bulb was carefully determined, and was found to be 0.00002804; its effect was allowed for. The effect of capillarity in depressing the mercury in the narrow tube was determined and taken into account. The volume of that part of the stem of the bulb which was not in the ice or vapour, as the case might be, was found to be 0.0003 of the whole, and was allowed for in the calculations. The change of volume in the bulb due to change of pressure was found to be negligible.

Gases.—The first gas experimented with was hydrogen. This was prepared from pure zinc, was washed with potassium permanganate solution and then with strong sulphuric acid, and was dried with phosphoric anhydride before it entered the previously exhausted bulb. The thermometer was successively filled and exhausted several times, in order to remove impurities, and was heated while vacuum to dislodge any gas clinging to the surface of the glass. Finally, the purified hydrogen was allowed to enter slowly until the required pressure was obtained.

Two sets of experiments were made with air. In the first set no effort was made to remove carbon dioxide, although the air was of course carefully dried. The readings were made by one of us alone, and, on account of

* A Paper read before the Royal Society.

Kind of thermometer.	Corrected pressure 0° .	In steam at about 100° , the temperature being accurately calculated.	Coefficient of expansion at constant volume $0-100^{\circ}$.	Temperatures calculated.			
				Chlorobenzene.	Aniline.	Quinoline.	Bromonaphthalene.
1. Hydrogen	—	712.56	—	131.6	183.9	236.35	—
2. Air I.	—	737.74	—	131.8	183.6	[234.9]	281.65
3. Helium	567.02	775.18	0.003665	132.2	184.1	236.9	[278.3]
4. Argon I.	517.02	706.06	0.003668	132.15	184.1	—	—
5. Argon II.	529.54	—	—	—	—	237.8	281.5
6. Air II.	511.68	698.79	0.003663	—	—	237.1	—
Air (Wiebe)	—	—	0.003670	—	184.3	235.9	—
Temperature (R. and Y.)	—	—	—	132.1	184.4	237.4	280.4

the numerous details to be attended to which actually require the attention of two observers to be put beyond question, are probably not as accurate as the other series. The second series had to be brought to a close after the pressures corresponding to 0° and the boiling-points of water and quinoline had been determined. In this series care was taken to use air free from carbon dioxide.

The helium used was some of that prepared and purified by Professor Ramsay. Its density was 2.13, that of oxygen being taken as 16.

The argon employed was prepared from atmospheric air by the method of Professor Ramsay. A large gas-holder was filled with air which had been slowly drawn through a long combustion-tube filled with red-hot copper. This gas was dried, passed again over the hot copper, and then over red-hot magnesium shavings until absorption of nitrogen ceased. By these processes a gas was obtained consisting of about equal volumes of argon and nitrogen. Passage of this gas, backwards and forwards, through tubes containing respectively red-hot magnesium, red-hot copper oxide (to remove the hydrogen given off by the magnesium on heating), soda lime, and phosphoric anhydride, failed to remove the nitrogen completely. Finally, with the aid of a circulating apparatus (See Rayleigh and Ramsay, *Phil. Trans.*, 1895, A. p. 212), which ensured the passage of all the gas over the hot magnesium, a product was obtained whose density was found to be 19.99, oxygen being 16. The thermometer was filled with this gas.

After the pressures exerted by the argon when the bulb was surrounded by melting ice and by the vapours of water, chlorobenzene, and aniline, successively, had been determined, the thermometer was heated in the vapour of quinoline, when for some unknown reason, it cracked. A new bulb, of the same glass and as nearly as possible of the same size, was prepared, cleaned, and filled with argon, and a second series of readings made.

Finally, the argon was replaced by air, and the second series of readings for air, referred to above, begun. On account of the closing of the laboratory for the summer, this series was not carried as far as would have been desirable.

Temperatures.—The temperature of the jacket, when filled with steam from water boiling smoothly under atmospheric pressure, was taken from Kohlrausch's "Physical Measurements." The samples of the boiling liquids used were re-distilled, and were found to pass over without a rise in temperature of more than a tenth of a degree, in three cases; of a fifth of a degree in the fourth case.

The results of our observations are laid down in the table. In three cases (3, 4, and 6) the reading was taken at 0° , as well as at the boiling-point of water; this enabled us to calculate the coefficient of expansion between these two points. The result is shown in the fourth column. The higher temperatures determined with these thermometers have been derived from the observed pressures by using the coefficients thus measured. As the barometric pressures differed, more or less, from the normal value, the boiling-points had to be reduced to normal pressure, for which operation we made use of the differences in Ramsay and Young's well-known tables

(*Chem. Soc. Journ.*, vol. xlvii., p. 640; vol. lv., p. 483). In calculating the temperatures of air thermometer I., where the reading at 0° had been omitted, and of argon thermometer II., where we did not take the reading in steam, we used the coefficients found with air thermometer II. and argon thermometer I., respectively, in the first case basing our calculations on the reading in steam. With the hydrogen thermometer, where the reading at 0° had not been taken, we accepted 0.003663 as the coefficient of that gas, and based our calculations of the temperatures again on the reading in steam.

Since the readings of the mercury surfaces, with the gas thermometer as well as the barometer, were taken on a millimetre scale, an occasional mistake in the final pressure of 0.1 or 0.2 m.m. is by no means excluded. Uncertainties of that amount do not, however, account for the differences between the results obtained with the different thermometers. The readings of air thermometer I. are, perhaps, somewhat less to be relied upon than the others, because they had to be observed, as was stated above, by one of us in the absence of the other. The boiling-point of bromonaphthalene, as determined with the helium thermometer, is also very uncertain, because the position of the mercury was not at all stable, probably on account of the difficulty of obtaining rapid and smooth boiling of the liquid. Yet, even if these values are not taken into account, the differences are very remarkable, especially with quinoline, and the agreement with Wiebe's result is also not quite satisfactory. Part of these differences may be due to impurity in the liquids used in the jacket. Pains were taken at the beginning of our experiments to have them quite pure, but as the values show, apparently, a tendency to rise, it may be that continuous boiling produced slight decomposition. In the case of bromonaphthalene this is more than possible. If more time had been at our disposal we should have tested the purity of our substances during the operations. As it is now, it would be unwise to draw conclusions from our figures about the exact behaviour of any of the gases used at high temperatures. The coefficients of expansion between 0° and 100° found for argon and helium agree very well with the values usually found for gases, and there is no indication of anything extraordinary happening to these gases at high temperatures. When argon thermometer I. was heated in the vapour of quinoline, a remarkable expansion of the gas was observed, continuing for two hours until a maximum value was reached; this gave an apparent temperature of 243.5° for the boiling-point of quinoline. On cooling the thermometer, however, it was found to be cracked, and some drops of quinoline were noticed inside the bulb. The measurements made in this case were therefore rejected, and a new series was begun with argon thermometer II., which gave a value about normal. How the quinoline could have found its way into the bulb while an interior pressure of about 970 m.m. existed within it, without the argon escaping rapidly at the same time, is not quite clear. It may be the vapour passed through the crack when the temperature was rather low, and that the condensing was closed by the later expansion of the glass.

For completeness sake, we give in the table the

Finally, it is a great pleasure to record our hearty appreciation of the kindly assistance of Professor Ramsay, at whose suggestion, and under whose supervision, these experiments have been conducted.

By R. M. DERLEY.

In Table I. all the best known elements are placed in the order of their atomic weights. To bring elements having similar properties into the same vertical lines, it has been necessary to leave many blanks. For instance, on the first line sixteen such blanks have been left, hydrogen and helium falling on the last two spaces.

The difficulty of placing argon in position in the Periodic Table is, however, much greater. Is it monatomic or diatomic? If monatomic, as is generally supposed, its atomic weight would place it between potassium and calcium—a position which would not agree with our present reading of the Periodic Law (*Nature*, Sept. 26, 1895, p. 537). Its refraction equivalent also indicates 20 rather than 40, and places it between fluorine and sodium, as shown on Table II. The only argument supporting the monatomic view is that derived from a consideration of the ratio of specific heats. This is often regarded as conclusive. Such, however, is not the case. Mr. J. W.

* "A New Diagram and Periodic Table of the Elements" (*Trans. Chem. Soc.*, 1893); "The Oxides of the Elements and the Periodic Law" (*Trans. Chem. Soc.*, 1894); "The Refraction Equivalents of the Elements and the Periodic Law" (*Trans. Chem. Soc.*, 1894).

TABLE I.

[illegible]

TABLE II.

[illegible]

Capstick (*Science Progress*, 1895, vol. iii., p. 281) says:—"After all, in our present state of ignorance regarding the status of the atom in the molecule, the argument drawn from the ratio of the specific heats is little more than an argument from analogy. The question at issue seems to be just the sort of case where the argument may break down, for argon differs in such a remarkable way from all other known substances that it would be unsafe to deny the impossibility of further eccentricities in the dynamics of its molecule."

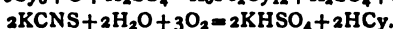
Under such circumstances would it not be well to follow the indications of the Periodic Law and refraction equivalents rather than a doubtful theory concerning the dynamics of the molecule?

ON THE TECHNICAL ANALYSIS OF CYANIDE WORKING SOLUTIONS.*

By W. BETTEL.

(Concluded from p. 287).

4. *Ferrocyanides and Sulphocyanides*.—In absence of organic matter, I have found that an acidified solution of a simple cyanide, such as KCy, or a double cyanide (as K_2ZnCy_4), i.e., solution of HCY, is not affected by dilute permanganate. On the other hand, acidified solutions of ferrocyanides and sulphocyanides, are rapidly oxidised—the one to ferrocyanide, the other to $H_2SO_4 + HCY$.



If now, the ferrocyanogen be removed as Prussian blue, by ferric chloride in an acid solution, the filtrate will contain ferric sulphocyanide and hydric sulphocyanide, both of which are oxidised by permanganate as if iron were not present; by deducting the smaller from the larger result, we get permanganate consumed in oxidising ferrocyanide, the remainder equal permanganate consumed in oxidising sulphocyanide.

The method of analysis is as follows (in presence of zinc):—A burette is filled with the cyanide solution for analysis, and run into 10 or 20 c.c. N/100 $K_2Mn_2O_8$ strongly acidified with H_2SO_4 until colour is just discharged. Result noted (a).

A solution of ferric sulphate or chloride is acidified with H_2SO_4 and 50 c.c. of the cyanide solution poured in. After shaking for about half a minute, the Prussian blue is separated from the liquid by filtration and the precipitate and filter paper washed. The filtrate is next titrated with N/100 $K_2Mn_2O_8$ (b).

Let c = c.c. permanganate required to oxidise ferrocyanide.

Then $a - b = c$.

(c) 1 c.c. N/100 $K_2Mn_2O_8$ = 0.003684 grm. K_4FeCy_6 .

(b) 1 c.c. N/100 $K_2Mn_2O_8$ = 0.0001618 grm. KCNS.

5. *Oxidisable Organic Matter in Solution*.—In treating spruit tailings, or material containing decaying vegetable matter, I offer the following method for testing coloured solutions:—

(a) Prepare a solution of a sulphocyanide, so that 1 c.c. sulphocyanide = 1 c.c. N/100 $K_2Mn_2O_8$.

(b) To 50 c.c. solution add sulphuric acid in excess, and then a large excess of permanganate, N/100. Keep at 60–70° C. for an hour. Then cool and titrate back with the KCNS solution.

Result O consumed in oxidising organic matter.

" O " " K_4FeCy_6 .

" O " " KCNS.

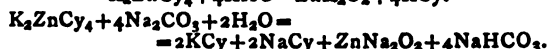
After estimating KCNS and K_4FeCy_6 , a simple calculation gives the oxygen to oxidise organic matter. This result multiplied by 9 will give approximately the amount of organic matter present.

In order to clarify such organically charged solutions, I shake them up with powdered quicklime, and filter; the solution is then of a faint straw colour, and is in a proper condition for analysis. In such clarified solution the oxidisable organic matter is no longer present, and the ferro- and sulphocyanogen estimations are readily performed.

6. *Alkalinity*.—Potassic cyanide acts as caustic alkali, when neutralised by an acid; the end-reaction, however, is influenced to some extent by the hydrocyanic acid present, and is therefore not sharp. We can, however, estimate—

By $\left\{ \begin{array}{l} \text{N/10 acid 100 \% KCy} \\ \text{N/10 acid 7.9 \% of } K_2ZnCy_4 \\ \text{N/10 acid 100 \% of zinc in} \\ \quad K_2ZnCy_4 \\ \text{N/10 acid 100 \% of Zn+K} \\ \quad \text{in } ZnK_2O_2 \\ \text{N/10 acid the } K_2O \text{ in} \\ \quad ZnK_2O_2 \end{array} \right\} \begin{array}{l} \text{With phenolphthalein} \\ \text{as indicator.} \\ \text{With methyl-orange} \\ \text{as indicator.} \\ \text{With phenolphthalein} \\ \text{as indicator.} \end{array}$

It will be necessary to point out the decompositions which result from adding alkali, or a carbonate of an alkali, to a working solution containing zinc.



Bicarbonates have no action upon potassic or sodic zinc cyanide.

Potassic or sodic zinc oxide (in solution as hydrate) acts as an alkali towards phenolphthalein and methyl-orange.



Calcic and magnesian hydrates decompose the double salt of K_2ZnCy_4 to some extent, but not completely, so that it is possible to find in one and the same solution a considerable proportion of alkalinity towards phenolphthalein, due to calcic hydrate in presence of K_2ZnCy_4 .

The total alkalinity as determined by N/10 acid with methyl-orange as indicator gives, in addition to those before mentioned, the bicarbonates. If to a solution containing sodic bicarbonate and potassic zinc cyanide be added lime or lime and magnesia, the percentage of cyanide will increase, the zinc remaining in solution as zinc sodic oxide.

7. *Ferricyanide Estimation*.—This is effected by allowing sodium amalgam to act for fifteen minutes on the solution in a narrow cylinder, then estimating the ferrocyanide formed by permanganate in an acid solution. Deduct from the results obtained the ferrocyanide and sulphocyanide previously found, 1 c.c. N/100 permanganate = 0.003293 grm. $K_6Fe_2Cy_{12}$.

8. *Sulphides*.—It rarely happens that sulphides are present in a cyanide solution; if present, however, shake up with precipitated carbonate of lead, filter, and titrate with permanganate N/100. The loss over the previous estimation (of K_4FeCy_6 KCNS, &c.) is due to elimination of sulphides.



or—



The hydrogen alone being oxidised by dilute permanganate in acid solution where the permanganate is not first of all in excess.

9. *Ammonia*.—If sufficient nitrate of silver be added to a solution (say 10 c.c.) to wholly precipitate the cyanogen compounds and a drop or two of normal hydrochloric be added in addition, the whole made up to 100 c.c., and

* A Paper read before the Chemical and Metallurgical Society, Johannesburg, S.A.R., August, 1895.

shaken, then filtered, and 10 c.c. filtrate distilled with 150 c.c. water from a tubulated flask, and the steam condensed in a Liebig's condenser (glass), the ammonia coming over may be readily estimated by colour test with Nessler solution and comparison with distilled water free from ammonia and standard ammoniac chloride solution containing 0.001 m.grm. per litre, treated with Nessler solution.

Then 10 c.c. taken diluted to 100 c.c.
10 " from 100 c.c. = 1 c.c. original
= 1000 m.grms., then every 1 c.c. standard solution of ammoniac chloride taken = 0.001 per cent NH_3 .

Urea, Oxamide, and Formates.—I am still investigating a method for the determination of these substances.

Although these reactions and processes take some time in describing, the whole of the operations can be performed within one hour, and once the operator has a practical knowledge of the process, the results, provided he is sure of the accuracy of the titre of his stock solutions, are most accurate. Most valuable information can in this way be obtained. I give a few instances of the analysis of working solutions:—

1. Solution (originally KCy) in contact with clean pyrites from Robinson concentrates for twenty-eight months with a limited supply of air:—

	Per cent.
Potassic ferrocyanide	0.77
Potassic sulphocyanide	0.14
Potassic cyanide	0.005
Potassic carbonate	0.33
Potassic formate, present but not estimated	—
Ammonia	0.21
Sulphides, absent	—
Sulphates, considerable, not estimated	—

2. Solution from treating dry crushed Robinson G. M. Company's ore without addition of neutralising agents after passing through zinc box:—

	Per cent.
Potassic cyanide	0.085
Potassic-zinc cyanide	0.25
Potassic-zinc hydrate	0.15
Potassic ferrocyanide	0.074
Potassic sulphocyanide	0.004
Potassic bicarbonate	0.566
Ammonia	0.808

3. As above, but with use of lime, not passed through zinc box:—

	Per cent.
Potassic cyanide, original 0.3 per cent	0.24
Potassic ferrocyanide	trace
Potassic ferricyanide	0.033
Potassic sulphocyanide	0.008
Ammonia	0.003
Calcic hydrate	0.067

4. As in No. 2, but with lime in small quantity, after passing zinc box:—

	Per cent.
Potassic cyanide, original 0.45 per cent	0.23
Hydrocyanic acid	0.04
Potassic-zinc cyanide	0.154
Potassic ferrocyanide	0.059
Potassic sulphocyanide	0.004
Potassic sulphate	nil
Potassic bicarbonate	0.547
Ammonia	0.006

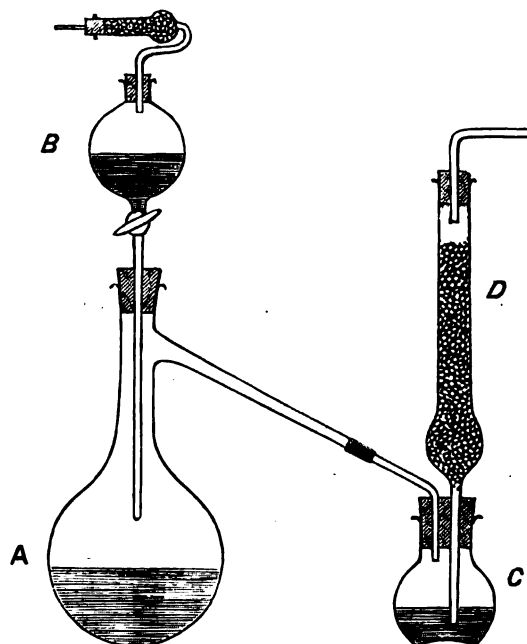
It will be unnecessary to quote more analyses. A better way will be for chemists and cyanide works managers to adopt the process and compare results from analysis of their different solutions.

APPARATUS FOR THE ESTIMATION OF SULPHUR IN IRON.

By E. J. READ, B.A.

IN the estimation of sulphur in iron the following apparatus is very efficient and convenient, and could probably be used for other purposes:—

The sample is placed in A, the acid in B. The side-tube of A is connected with the wash-bottle C, to which a calcium chloride tube D, filled with glass beads, is attached. The tube of D dips a regulated distance below the surface of the absorbing liquid, so that this is forced up among



the beads by the passage of the evolved gas, and a most efficient absorption is obtained with the use of only a small quantity of absorbent. If the inlet tube of C dips below the surface of the liquid, it must be raised before disconnecting the apparatus, to prevent loss of liquid. The operation is preferably conducted under reduced pressure, and a current of pure air may be run through the apparatus at the conclusion to sweep out the remaining traces of gas from A.

BOILING-POINT AND THE GENESIS OF THE ELEMENTS.

By C. T. BLANSHARD, M.A.

IN a late number of the CHEMICAL NEWS (vol. lxxi, p. 285) I drew a parallel between the elements and certain organic compounds, establishing a connection between melting-point and periodic groups on the one hand, and melting point and structure on the other. In the following article I hope to show that the physical property of volatility is equally valuable as a clue to the relationship of the elements to one another.

Data as regards the boiling-points of elements are still very defective; but, if we examine into the elements group by group, we shall soon see that definite laws of volatility hold. Thus we have in—

Group.	Element.	B. p.	Diff.	Observer.
I.	Na	742°	75°	Perman.
	K	667°		Perman.
II.a.	Zn	940°	170°	Violle.
	Cd	770°	213°	Carnelley.
	Hg	357°	—	Regnault.
	Mean diff. ..		191°	

In Groups II., III., &c., there are not data enough.

Group.	Element.	B. p.	Diff.	Observer.
V.	N	-194°	483°	Wroblewski; Olszewski.
	P	+289°		Dalton; Pelletier.
	As	360°	71°	Engel.
	Sb	1440°	1080°	Carnelley & Williams.
	Bi	1700°	340°	
	Mean ..		496°	Mensching and V. Meyer; Biltz and V. Meyer.
VI.	O	-181°	629°	Olszewski; Wroblewski.
	S	+448°		Regnault.
	Se	680°	232°	Carnelley.
	Mean ..		430°	
	Te	?		
VII.	F	?	97°	Regnault.
	Cl	-34°		
	Br	+63°	121°	Pierre; Stas; van der Plaats.
	I	184°	—	Ramsay and Young.
	Mean ..		109°	

The values are from Landolt and Börnstein, "Physikalische-chemische Tabellen," 1894; except that for iodine, which is from the last edition of "Watts' Dict. Chem."

From the above tables we may fairly induce the following laws for the elements regarding boiling-point:—

1. In the metallic groups (*i. e.*, I. to IV. inclusive) the volatility varies directly as the atomic weight, whilst the differences between the successive boiling-points are more or less constant.
2. In the non-metallic groups (*i. e.*, V. to VII. inclusive) the volatility varies inversely as the atomic weight, whilst the differences between successive boiling-points alternate to a marked degree.
3. The mean differences gradually increase up to Group V., or group of the highest general atomicity, and then again gradually diminish.

Let us now, with these facts in view, see what maintains in various groups of organic compounds, taking some of less, others of greater complexity.

Karl Windisch, in his "Beziehungen zwischen den Siedepunkt u. der Zusammensetzung Chem. Verbindungen," Berlin, 1889, quotes the researches of the following: (the abbreviations are those used in "Watts' Dictionary")—Kopp (A. 41, 79; A. Supp. 5, 321; A. 96, 1; 50, 79; Schorlemmer (A. 161, 281); Linnemann (A. 162, 41); Hantsch (A. 115, 36); Schmidt (B. 5, 597; 6, 498); Michaelis (B. 8, 499); Goldstein (J. R.); besides Naumann, Schreiner, Henry, Denzel, Sabaneyeff, Kahlbaum, Staedel, and Mills. He finds that all these researches point to the comparative constancy of the differences between the boiling-points in various organic series. Each

organic series, he shows, has its own constant difference for every increment of CH_2 . Thus for (1) 25 alcohols he finds the average difference to be 19.5°; (2) 71 fatty acids, average diff. = 21.5°; (3) mercaptans, average diff. = 29°.

Windisch remarks on these figures that "the differences in nearly all cases are very near the average differences given." But the facts really point to a different and most interesting conclusion.

I will take certain organic series which are tolerably complete as to boiling-points, besides being well authenticated. The temperatures are from Victor Meyer and Paul Jacobson, "Lehrbuch der organ. Chemie" (Veit and Co., Leipzig, 1893). I have added the differences, selecting only the normal compounds to base them upon.

1. Normal Paraffins.

Formula.	B.-p.	Diff.
C_4H_{10}	1	0
C_5H_{12}	37	36
C_6H_{14}	69	32
C_7H_{16}	98	39
C_8H_{18}	125	27
C_9H_{20}	150	25
$\text{C}_{10}\text{H}_{22}$	173	23
$\text{C}_{11}\text{H}_{24}$	195	22
$\text{C}_{12}\text{H}_{26}$	214	19
$\text{C}_{13}\text{H}_{28}$	234	20
$\text{C}_{14}\text{H}_{30}$	252	18
$\text{C}_{15}\text{H}_{32}$	270	18
$\text{C}_{16}\text{H}_{34}$	287	17
$\text{C}_{17}\text{H}_{36}$	303	16
$\text{C}_{18}\text{H}_{38}$	317	14
Average ..	23.3	

2. Normal Primary Alcohols.

Formula.	B.-p.	Diff.
$\text{CH}_3.\text{OH}$	66	0
$\text{C}_2\text{H}_5.\text{OH}$	78	12
$\text{C}_3\text{H}_7.\text{OH}$	97	19
$\text{C}_4\text{H}_9.\text{OH}$	117	20
$\text{C}_5\text{H}_{11}.\text{OH}$	138	21
$\text{C}_6\text{H}_{13}.\text{OH}$	157	19
$\text{C}_7\text{H}_{15}.\text{OH}$	176	19
$\text{C}_8\text{H}_{17}.\text{OH}$	195	19
$\text{C}_9\text{H}_{19}.\text{OH}$	213	18
$\text{C}_{10}\text{H}_{21}.\text{OH}$	231	18
Average ..	19.5	

3. Normal Primary Aldehyds.

Formula.	B.-p.	Diff.
CH ₃ .COH	21	0
C ₂ H ₅ .COH	49	28
C ₃ H ₇ .COH	73	24
C ₄ H ₉ .COH	102	29
C ₅ H ₁₁ .COH	128	26
C ₆ H ₁₃ .COH	155	27
C ₇ H ₁₅ .COH	171 ?	16 ? (25 ?)

Average .. 26.5

4. Normal Fatty Acids.

Formula.	B.-p.	Diff.
H.CO ₂ H	101	0
CH ₃ .CO ₂ H	118	17
C ₂ H ₅ .CO ₂ H	141	13
C ₃ H ₇ .CO ₂ H	162	21
C ₄ H ₉ .CO ₂ H	185	23 (exceptional).
C ₅ H ₁₁ .CO ₂ H	205	20
C ₆ H ₁₃ .CO ₂ H	223	18
C ₇ H ₁₅ .CO ₂ H	236	13

Average .. 18

5. Primary Ethyl Esters.

Formula.	B.-p.	Diff.
HCO ₂ .C ₂ H ₅	55	0
CH ₃ CO ₂ .C ₂ H ₅	77.5	22.5
C ₂ H ₅ CO ₂ .C ₂ H ₅	99	21.5
C ₃ H ₇ CO ₂ .C ₂ H ₅	121	22
C ₄ H ₉ CO ₂ .C ₂ H ₅	145	24 (exceptional).
C ₅ H ₁₁ CO ₂ .C ₂ H ₅	167	22
C ₆ H ₁₃ CO ₂ .C ₂ H ₅	187	20
C ₇ H ₁₅ CO ₂ .C ₂ H ₅	206	19
C ₈ H ₁₇ CO ₂ .C ₂ H ₅	227.5	21.5

Average .. 21.5

6. Normal Primary Mercaptans.

Formula.	B.-p.	Diff.
CH ₃ .SH	6	0
C ₂ H ₅ .SH	36	30
C ₃ H ₇ .SH	67	31
C ₄ H ₉ .SH	97	30

Average .. 30.3

7. Normal Primary Ketones.

Formula.	B.-p.	Diff.
(CH ₃) ₂ .CO	56	0
(C ₂ H ₅) ₂ .CO	103	47
(C ₃ H ₇) ₂ .CO	144	41
(C ₄ H ₉) ₂ .CO	181	37
(C ₆ H ₁₁) ₂ .CO	227	46
(C ₆ H ₁₃) ₂ .CO	264	37

Average .. 42

In the above series we notice:—

1. Following Windisch's method, the average differences in boiling-point are as follows:—

	Mean diff.
1. Normal primary acids	18
2. " " alcohols	19.5
3. " " ethyl esters	21.5
4. " " paraffins	23.3
5. " " aldehyds	26.5
6. " " mercaptans	30.3
7. " " ketones	42

2. The more complex the members of any series, *i.e.*, the more they deviate from the simple structure of the water type, the greater the mean difference.

3. In all the above series the differences alternate with more or less regularity; but in the series of least differences the alternation is least, the differences approaching a constant; whilst the series of greatest differences show the greatest alternations.

In all organic series the volatility varies inversely as the atomic weight.

With the above-mentioned exception, the laws relating to the difference of boiling-point of organic compounds, and the alterations of the same, show a close connection with Laws 1 and 2 applying to the elements.

A comparison of the data so far brought to bear on the subject and the laws induced from these data, leads us to the conclusion that, of the elements, Groups I. to IV.—of general valency one to four—are less highly evolved than Groups V. to VII.—of increasing valency with regard to oxygen, and of decreasing valency with regard to hydrogen.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 286).

On the Methods used to ascertain whether Solid Bodies were Present in or Absent from Chlorate, Perchlorate, and Chloride of Potassium.

To verify the absence or presence of iron, manganese, copper, aluminium, and silicon, in chlorate, perchlorate, and chloride of potassium, I argued from the following facts:—

Chlorate and perchlorate, when dissociated by the action of heat in a pure polished platinum dish, are clearly transformed into chloride and oxygen without liberating a trace of chlorine. The evolution of chlorine, detected by all chemists during the decomposition of these salts by the action of heat, is due to the presence of foreign bodies in the compounds submitted to dissociation, and especially to the presence of iron, manganese, copper, aluminium, or silicon.*

* In a memorandum added to the chapter on the "Preparation of Pure Chlorate, Perchlorate, and Chloride of Potassium," I describe

Fused chloride of potassium is *colourless*, or more or less coloured *red, pink, or green*, according as it is free from or contains iron, manganese, or copper.

When heated beyond its fusing-point, colourless chloride of potassium—except it contains aluminium, silicon, or calcium—volatilises without leaving a trace of residue.

If the quantity of aluminium and silicon, in the form of aluminous silicate or silica, exceeds about 1-5000th of the whole in weight, the chloride of potassium when melted immediately shows brilliant specks floating on the liquid, caused by alumina or silica, or silicate of aluminium. In the other case, one only sees the brilliant specks appear on volatilising chloride by heat, when the proportion of alumina or silica, or silicate of aluminium, is brought to about 1-5000th of the weight of chlorine.

If the silicon is in the chloride in the form of silicate of potassium or sodium, as is generally the case, the chloride when melted is a homogeneous liquid, even though the proportion of silicate be raised to a considerable percentage of the weight.

Dull platinum, and even this metal when polished, are wetted by melted chloride of potassium. Thus, when volatilising a chloride containing either silicate of potassium or silicate of sodium, you may see that—in proportion as it evaporates—the chloride leaves *concentric circles* of solid silicate, which keep increasing in thickness.

The appearance of these concentric circles is so constant that one can rely on them, as I have done during the preparation of pure chlorate, to judge of the degree of purification as regards the elimination of silica combined with potassium and sodium.

When applying this method of research to the chloride obtained from so-called pure chlorate of potassium from chemical manufactories, I have relied on the same rings to show me the large quantity of solid matters left on evaporation.

To verify the above facts, I have volatilised the chloride of potassium in a concave lid of a large pure platinum retort with wide flat edges, holding 10 or 12 grms. of melted chlorate. This lid rested by its border on a ring made of very thick platinum wire, supported by *three* blocks of fire-clay. These blocks were arranged so as to form a passage shut on one side, opened on the other, intended to hold a coal-gas blowpipe worked by bellows, and to serve for carrying off the products of combustion. The coal-gas and air blowpipe was arranged so as to give the highest possible temperature at the *centre* of the platinum lid, whilst raising its flat rim to a red heat so as to unite it to the ring which supported it. The flat rim completely covering the ring, the products of combustion could not escape around the dish, and were obliged to pass away by the upcast channel.

When working the apparatus in a closed room, the air of which has been purified by remaining still for at least twelve hours, one can go on with the volatilisation of the chloride without it being necessary to place, at a certain distance above the lid, a sheet of platinum to prevent the dust, known to be always in air in motion, from falling into the chloride. I will add that I have proceeded in this manner during the numerous *qualitative analyses* I have made, as well for ascertaining the degree of purity of the chloride got by dissociating so called pure chlorate supplied by dealers in chemicals, as to judge of the state of progress in purifying the chlorides got from the decomposition of those chlorates of potassium.

When I have been making a *quantitative analysis* I have taken care to suspend, by a platinum wire, a large sheet of this metal in a very inclined position, and near enough to the surface of the dish to diminish the current which exists whatever one may do, and to prevent the projection into it of foreign bodies by draughts.

The method I used to ascertain whether chlorine were present in or absent from oxygen produced by the decomposition of absolutely pure chlorate and perchlorate of potassium by heat.

By regulating the blowpipe, both for the amount of gas burnt and for its position, one can volatilise in free air about 10 grms. of chloride of potassium in *from eighteen to twenty minutes*, by the method I have just described. On the other hand, it requires at least *thirty minutes* when placing a large sheet of platinum at a great inclination above and near the surface of the evaporating dish. In this case a certain part of the volatilised chloride is deposited in a crystalline, transparent, and colourless state, in the centre of the sheet, surrounded by a snowy border. One could use this deposit for obtaining chloride free from all solid bodies, if it were not easier and more certain to obtain it free from all solid bodies, and from the sodium of the air, by the method described above, which I have twice done on a large scale, as I shall describe further on.

I have compared the result arrived at by this quick method with that very much longer one I described in my "New Researches on the Laws of Chemical Proportions," and which consists in performing the volatilisation in a platinum boat, placed in a porcelain tube covered inside with platinum, and raised to white heat, and causing a current of dry nitrogen to pass through it.

When applying purified nitre with the greatest care to part of the chloride in which I had found, by the latter method, 0.00056 grm. of solid residue, I found by the new method 0.00060 grm. per 10 grms. experimented on. Both methods are evidently of equal value.

To finish this description I ought to add that experience has shown me that one cannot rely on the weight of the platinum vessel keeping constant when heated in the *coal-gas and air blowpipe*. I have often found the weight slightly increased, but more often decidedly decreased. When one wishes to get as accurate results as possible, one must weigh the platinum vessel on which one has evaporated the chloride, and weigh it again after having allowed hydrofluoric acid mixed with its own volume of water to remain in the *cavity in the cold*; and then hydrochloric acid diluted to 1-20th; and lastly, after having washed it enough with pure water. Under these conditions pure platinum does not change in weight.

By taking the difference between the first and second weight of the platinum vessel when heated to white heat and then cooled under a bell-jar in air of the same dryness, as the weight of the residue, one is bound to get a result as accurate as a research of this nature permits of.

To look for *calcium* in the chlorate and chloride of potassium I employed spectrum analysis; but the quantity of this metal being seldom enough to be seen in the compounds put into the flame, I have, after having transformed the chlorate into chloride, volatilised it down to a few hundredths of its volume. I then put the residue into a Bunsen flame or into an oxyhydrogen blowpipe flame, to look for the characteristic lines of the calcium spectrum. By doing this, one is easily convinced of the extreme difficulty of obtaining chlorate or chloride of potassium absolutely free from calcium.

On the Preparation of Chlorate of Potassium.

After having ascertained that, by means of a very dilute solution of sulphhydrate or hydroxide of potassium, one can transform the silicon and sodium in chlorate of potassium to a *silicate*, I have, on two different occasions, proceeded with the purification of commercial chlorate, which I had submitted to a preliminary analysis, working the first time on *three kilograms*, and the second time on *two kilograms* of this salt from different sources. The chlorate to be purified contained iron, manganese, copper, a great deal of sodium, silica, aluminium, magnesium, calcium, chlorides and sulphates, as well as organic dust. I effected the purification in the following manner:—

To a sufficient quantity of water, kept at about 100° in two large porcelain dishes, was added, to saturation, the powdered chlorate, and the solution was filtered to get rid of the dust in suspension. The filtered liquid, having been again brought to about 100°, received an excess of a

dilute solution of sulphhydrate of potassium,* and was filtered immediately. On suddenly cooling it the solution precipitated a salt in small *pink* flakes. The mother-liquor, which was coloured, was completely separated. The salt was put into a large shallow funnel, fitted with a clean linen plug, and a smooth ground-glass cover with a hole in it. The funnel was fitted on to a large flask with two tubes communicating with a water-pump. After straining the salt in pure air it was sprinkled with iced water containing about one per thousand of sulphhydrate of potassium, keeping the pump at work until the chlorate was rendered completely colourless. The sulphhydrate solution was followed by pure iced water, to remove the alkali and foreign salts as much as possible.

The colourless saline flakes were finely powdered in a Wedgewood mortar, and the powder was replaced in the large funnel and washed afresh with pure iced water.

The chlorate, when treated thus, had a very decided sodic reaction. It was saturated with water at 100°. The solution, not being clear, was filtered, and to the liquid—heated to re-dissolve all the chlorate which had been crystallised by cooling—was added a solution of sulphhydrate in sufficient quantity to give it an *alkaline reaction*. The liquid was neither cloudy nor coloured, and the chlorate which was precipitated on suddenly cooling it was in fine colourless flakes.

The salt was strained and washed with a wash-bottle, first with iced water containing one per thousand of sulphhydrate of potassium, and then with pure iced water. The sodium lines were distinctly visible on analysis, but by no means so clearly as in the case of the chlorate from which the salt was made.

When dissolved in water it did not cloud a solution of chloride of barium, but it did very sensibly nitrate of silver.

I repeated a third time, in porcelain, the treatment I have just described, and, although I was obliged to work in the soda-contaminated air of the laboratory, the chlorate showed the sodium characteristics in a Bunsen burner so faintly that it was necessary to resort to spectrum analysis before being able to detect with certainty the presence of sodium in it.

The solution of salt no longer clouded nitrate of silver, but the chlorate, when decomposed by heat, evolved a sensible amount of chlorine, and the chloride formed from it—when volatilised by the method mentioned above—left a small residue in which I detected the presence of silica, potassium, sodium, aluminium, and calcium.

Having learnt, as I have described above, by preliminary trials, that, by continuing the treatment in porcelain

or glass tubes, one introduces as much silica and sodium into the chlorate as the use of sulphhydrate of potassium enables one to eliminate from it, I continued the operations entirely in platinum, and, as far as possible, in enclosed and purified air. For this purpose I dissolved it in boiling water in a large platinum retort with a lid, *the neck of which contained a large cotton plug washed with a mixture of ether and alcohol, dried, and then soaked in a saturated solution of chlorate of potassium.*

As soon as the water was saturated the liquid was made alkaline by sulphhydrate of potassium, and immediately cooled by plunging the retort into running cold water, and finally into snow. By inclining the retort to one side the mother-liquor was drained off by the opening in the neck of the dome, from which the cotton plug soaked in the chlorate solution was removed. By plunging a hard rubber-tube, treated successively with a dilute boiling solution of pure potassium with dilute acetic acid, and then with pure water, into the saline mass, the remaining mother-liquor was drawn by suction; this was replaced several times with small quantities of iced water containing hydrate of potassium. and then with pure iced water, until the liquor was quite neutral to litmus-paper.

After this *fourth* treatment, the salt, when introduced into a Bunsen flame, gave it a *pale blue* colour. At the time of making this experiment the air of the large room in which I was working gave no trace of the sodium spectrum; nevertheless, after the introduction of chlorate on the end of a loop of fine platinum wire recently heated to redness, the sodium line was seen, though very faintly.

Several grms. of this chlorate were reduced to chloride by the action of heat, and this was volatilised by the method mentioned above. When it was reduced to about 1-tenth of its original volume, the residue began to form very weak concentric rings of silicate fusible at the highest temperature. On carrying volatilisation to completion, the chloride was evaporated *without depositing any brilliant specks, though a series of rings, very thin, colourless, transparent, and very fusible, was deposited.* These little rings, when heated in the oxyhydrogen blow-pipe, gave it a *violet* colour. Spectrum analysis of the flame enabled me to detect the presence of the sodium line, side by side with the potassium spectrum, but the characteristic calcium lines were entirely absent, although the temperature was high enough to melt the platinum in which the chloride was volatilised.

In face of this result I repeated the solution and crystallisation of the chlorate in water containing one per thousand of hydroxide of potassium, made from nitre as pure as I could get it. I washed the salt first in this same alkaline iced water, and then with pure iced water, working, as I have mentioned above, in a large room *apart from the laboratory.*

The chlorate from this *fifth* treatment coloured a Bunsen flame *pure pale blue*, and on spectrum analysis of the flame I could not see the sodium line any stronger than in air without chlorate.

I once more reduced part of the salt to chloride. Its dissociation was effected without evolving chlorine. Ten grms. of absolutely colourless and *neutral* chloride were volatilised without leaving a trace of residue visible under the microscope.

Fearing, nevertheless, the presence of traces of dust and alkali in this salt, I made the solution in almost boiling pure water, and I passed the saturated liquid through small filter-papers, in platinum funnels, purified with water acidulated by hydrofluoric and hydrochloric acids, and then with pure water. The filtered liquids were received into platinum vessels, *all of which were placed on smooth sheets of glass, and covered with a bell-jar, with a ground and polished edge and with its surface moistened, to stop contamination by dust.*

After filtration and carefully washing the filters with water, I was unable to detect on the surface of the paper the slightest trace of dust, or any deposit whatever.

The filtered solution, which was no longer saturated a

* The preparation of a solution of hydroxide and sulphhydrate of potassium, as free as possible from sodium, is a very delicate operation. I procured the compounds used in my researches by means of oxide of potassium made by Wöhler's method,—that is to say, by heating a mixture of nitre and pure copper in excess, in a large copper crucible made by electrolysis from pure sulphate of copper. The nitre came from nitrate purified for powder-making. I crystallised it *three times* in a one per thousand solution of sulphhydrate of potassium, *seven times* in a one per thousand solution of hydroxide of potassium, *working in enclosed and purified air*, in a large platinum retort, and *hna ly twice* in pure water. The nitrate, which was crystallised three times in the sulphhydrate converted into chloride, *was completely volatilised*; but when put into a flame it showed, on spectrum analysis, the sodium line with a comparatively great intensity. It therefore still contained some sodium, without doubt in the form of a nitrate. After having crystallised it *four times* more in water made alkaline by hydroxide of potassium, and *twice* in pure water, it gave the flame a blue tint slightly tinged with violet, and showed the sodium line *very faintly* until it was completely volatilised, which was done with very great rapidity. I must confess that when working with nitre already purified I was not able to prepare nitrate of potassium *absolutely* free from sodium by means of successive crystallisations in alkaline and pure water. But, judging by the faintness of the sodium line, the amount of sodium held by the nitre did not exceed the amount often found in dry air, when undisturbed for eighteen hours in a very large room. The solution of hydroxide of potassium resulting from the absorption of water by oxide of potassium always contained copper, owing to the action of copper on nitre. The separation of copper from the solution was effected by means of a proper quantity of hydrosulphuric acid. The transformation of hydroxide free from copper into sulphhydrate, and the preservation of the hydroxide and sulphhydrate solutions, are done in closed platinum vessels, to protect them from contact with the air.

boiling-point, was put back into the large platinum crucible, the neck of which reached very far into a flask, and was concentrated down almost to dryness, and then quickly cooled. The mother-liquor, although colouring a flame pale blue and not showing the sodium line, was entirely separated. The chlorate was dried in the platinum crucible covered by a lid, the long neck of which reached far into a flask full of purified air, by placing the crucible in an air-bath heated to 100°.

Out of five kilograms of commercial salt, worked upon in two operations, I only saved four hundred grms. of chlorate that I could consider pure,—that is to say, only eight per cent of the weight of salt used.

I made, with the greatest care, an experiment on the chlorate obtained in each operation, to ascertain the quantity of solid matters left after evaporating the chloride made by dissociating it in a covered platinum retort. I took 5.007 grms. of chloride from the first chlorate, and 8.190 grms. of chloride from the second chlorate; in both cases the material experimented upon was volatilised without leaving a trace of residue, I do not say "weighable," but not even visible under the microscope.

These two researches, the execution of which was as laborious as delicate, enable me to state that under suitable conditions, it is possible, contrary to my previous opinion, to obtain chlorate, and therefore chloride, of potassium absolutely free from sodium and solid matters.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Special Meeting, December 13th, 1895.

Prof. REINOLD, Vice-President, in the Chair.

THE Resolution with reference to the change in the amount of the life-composition fee, passed at the Special General Meeting held on November 22nd last, was confirmed.

The Ordinary Meeting was then held.

Dr. JOHN SHIELD read a paper on "*A Mechanical Device for Performing the Temperature Corrections of Barometers.*"

The form of barometer to which the author has adapted his device is that devised by Dr. Colley; it is intended for general laboratory use, and is capable of being read to within 0.1 m.m. The barometer tube can be moved in a vertical direction, so that the lower meniscus can be adjusted to the zero of the scale. Attached to the barometer tube is a thermometer with a horizontal stem, passing in front of a scale which is fixed to the vertical scale of the barometer. The graduations of this thermometer scale, with the exception of the one passing through the 0° C. mark on the thermometer, are inclined to the vertical, and are so spaced that the reading opposite the end of the mercury column of the thermometer gives directly the correction to be applied to the observed height of the barometer (B_1) in order to obtain the reduced height (B_0); that is, the reading on the thermometer scale gives the value of $B_1(\beta - \gamma)t$; where β and γ are the coefficients of expansion of mercury and of the material of which the barometer scale is composed respectively, and t is the temperature.

Mr. BOYS admired the simple method the author had adopted for plotting the corrections, and said that he always felt that the trouble involved in applying small corrections ought, if possible, to be avoided, or the corrections would often be omitted.

Mr. APPLEYARD advised the placing of the bulb of the thermometer within the barometer tube.

Dr. SHIELD, in his reply, said as the barometer was only intended to read to 0.1 m.m., the placing of the thermometer within the tube did not appear necessary.

A paper by Prof. RÜCKER on "*The Resistance of Vertical Earth-air Currents in the United Kingdom*" was, in the absence of the author, read by Mr. KAY.

In a paper read before the British Association, at Oxford, Dr. Schmidt stated that he had expanded the components of the earth's magnetic force in series, and had deduced expressions, two of which give the magnetic potential on the surface of the earth, in so far as it depends on (1) internal and (2) external forces. "The third series represents that part of the magnetic forces which cannot be expressed in terms of a potential, but must be due to electric currents traversing the earth's surface."

Dr. Schmidt concluded that such currents amount on the average to about 0.1 ampère per square kilometre. The author has tested this conclusion, drawn from the state of the earth as a whole, by means of an examination of the line integral of the magnetic force round a re-entrant circuit, taken in the United Kingdom. The necessary data have been obtained from the results of the magnetic surveys for the epochs 1886 and 1891, carried out by the author and Dr. Thorpe. Two circuits called the α and β circuits were selected, having their greatest extension north and south and east and west respectively. The work done by a unit magnetic pole on traversing these circuits was calculated for the epoch 1886 by means of the terrestrial lines found for that date, and also for the epoch 1891 by means (1) of the same lines when due allowance was made for secular change, and (2) of the independent set of lines found by aid of the 1891 survey. The same calculation was made for a third circuit (γ) using, instead of the calculated terrestrial lines, the true values of the forces and delineations as deduced from the nearest stations. The following table gives the results in ampères per square kilometre:—

	α .	β .	γ .
1886	-0.026	-0.004	—
1891 (1)	+0.001	-0.005	—
1891 (2)	—	—	-0.008

From these figures the author concludes that there is not, in the United Kingdom at any rate, a vertical current amounting on the average to 0.1 per square kilometre.

Mr. WATSON said a few words on the difficulty experienced in determining the line integral in South Wales, due to the presence of closed curves.

The Society then adjourned till January 24th, 1896.

EDINBURGH UNIVERSITY CHEMICAL SOCIETY.

Second Ordinary Meeting, Monday, December 2nd, 1895.

Dr. MACKENZIE in the Chair.

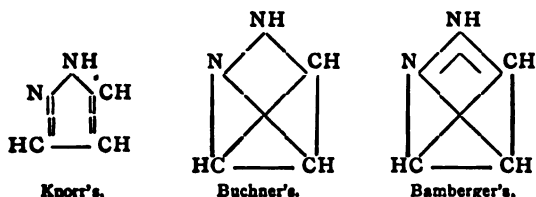
Dr. MACDONALD read a paper on the "*Constitution of Pyrazole*," being an account of the work done by himself at Jena, of which the following is an abstract.

It was pointed out that three constitutional formulæ had been proposed for pyrazole, and these by Knorr, Buchner, and Bamberger, modelled on the benzene formulæ of Kekulé, Claus, and Baeyer respectively. For derivatives with a substituting atom or group on one of the nitrogen atoms an unsymmetrical formula accounts for all observed phenomena; but otherwise, according to results obtained by him in the Chemical Laboratory at Jena, each of the above-mentioned formulæ is inapplicable.

A methylpyrazole, necessarily 3- or 5-methylpyrazole, which showed no trace of isomers, was prepared synthetically. Next both 3- and 5-methylpyrazole were prepared analytically by burning away, by means of permanganate

of potash, the phenyl-group from 1-phenyl-3-methylpyrazole and 1-phenyl-5-methylpyrazole respectively—a reaction which was found to go better on the introduction of a nitro-group into the benzene ring, and subsequent reduction. These analytically prepared substances were both identified with the synthetically prepared methylpyrazole by the boiling-point and by the preparation of four derivatives—the corresponding pyrazole carboxylic acid and nitromethylpyrazole, and the double salts with AgNO_3 and HgCl_2 . Of some twenty derivatives of the synthetical product, these four had been selected as the best adapted for the identification.

According to this result, the molecule is synthetical, and each of the three formulæ—



is impossible.

The difficulty of disposing of the H atom, which in the above formulæ is attached to a nitrogen atom, makes it hard to say what the correct formula may be. It seems that this H atom must move from atom to atom in the ring. As to whether it visits every atom in the ring, or only the two nitrogen atoms and the middle carbon atom, or the two nitrogen atoms merely, cannot at present be decided.

Third Ordinary Meeting, Monday, December 9th, 1895.

Dr. MACKENZIE in the Chair.

DR. MARSHALL read a paper on "Optical Activity and Crystalline Form," of which the following is an abstract.

In an ordinary ray of light the vibrations take place successively in all possible directions perpendicular to its axis. By certain means it is possible to restrict the vibrations to one particular plane. The ray is then said to be plane-polarised.

This may be accomplished by means of certain crystals, such as calc-spar or tourmaline, which have the property of double refraction.

While studying the action of plane-polarised light on crystalline plates, Arago noticed that a plate of quartz cut at right-angles to the optic axis, rotates the plane of polarisation of light transmitted through it. He further noticed that some specimens of quartz rotate the plane of polarisation to the right, and some to the left. This remarkable phenomenon was carefully investigated by Biot, who deduced the following laws:—

1. The amount of rotation is proportional to the thickness traversed by the ray.
2. The rotation effected by two plates is the algebraic sum of the rotations produced by each separately.
3. The rotation is approximately proportional to the inverse square of the wave-length of the light used.

Biot soon discovered that many organic liquids, solutions, and vapours also rotate the plane of polarisation.

It was soon noticed that the optical activity of crystals was a quite distinct phenomenon from the optical activity of liquids. Thus Herschel, by dissolving quartz in fused potash, found that the optical activity disappeared. Herschel also observed that there was a connection between the direction of rotation and the arrangement of the plagioclinal faces on quartz crystals. Here the optical activity is due to crystalline structure.

In the case of liquids, solutions, and gases, Biot's experiments on oil of turpentine showed that here the optical activity is due to individual molecules.

Substances which are optically active only in the solid state, such as quartz, sodium chlorate, sodium bromate, Schlipf's salt, cinnabar, &c., are without exception isotropic or uniaxial. Substances which are optically active only in the liquid state, such as tartaric acid and its salts, are all compounds of carbon.

Pasteur carefully investigated the two optically active tartaric acids. When in solution, they rotate the plane of polarisation equally, but in opposite directions. The crystals are hemihedral and enantiomorphous; though this is the case with all optical isomers, the converse is not true, since many substances are known which, though crystallising in forms devoid of planes of symmetry, are not optically active in solution.

Some substances, such as strychnine sulphate and rubidium tartrate, are optically active both in the crystalline state and when dissolved.

Wyruboff has studied numerous allied compounds, and has tried to apply Mallard's theory of the rotatory power of crystalline substances to solutions. He arrives at the following conclusions:—

1. That the rotatory power of substances in solution, like the rotatory power of crystalline bodies, depends on the structure of the crystalline molecule, as distinguished from the chemical molecule.
2. In solution the crystal molecules are not broken up, and therefore there can still less be dissociation into ions.

CORRESPONDENCE.

ON THE PLACE OF HELIUM IN THE CLASSIFICATION OF ELEMENTS.

To the Editor of the Chemical News.

SIR,—In the *CHEMICAL NEWS* (vol. lxxii., p. 291) Mr. Wilde accuses me of loose arithmetic and looser assertions. This charge is founded on a short report of some extempore remarks which I made at the Physical Society on November 22nd, during the discussion of a paper by Dr. Johnstone Stoney.

My first impulse on reading that report was to write a letter explaining that it was inaccurate. On second thoughts I refrained, for the arithmetical mistakes were so obvious that I thought every reader who knew anything of the subject would put them down as a reporter's or printer's error. The figures given were certainly not those which I wrote on the black board. If they had been correctly given there would have been little difficulty in understanding my previous statement, notwithstanding its very condensed nature.

My object was to show that if the two new gases of which helium is probably composed are really analogous to the alkaline metals, as Prof. Runge's photographs of the spectra seemed to indicate, there was no serious difficulty in placing them in the same group. It is evident that the difference of atomic weight between hydrogen and lithium is only 6; between lithium and sodium it rises to 16; and after two terms it again rises to 24. Subsequently it is probable that the difference is still further increased. There would therefore be no difficulty in supposing that the first difference might be less than 6.

Excepting in their bearing on the position of helium, the views expressed by me are by no means new. As far back as 1853 I showed (*Phil. Mag.*, May, 1853) that the atomic weights of several series of analogous elements differed by certain increments like those in the well-known organic series, and I drew special attention to the occurrence of the numbers 16 and 24. In an address to the Chemical Section of the British Association, in 1883, speaking of the atomic weights in Mendeleeff's table, I observed that "those in the vertical series differ from one

another, as a rule, by the before-mentioned multiples of 8, namely, 16, 16, 24, 24, 24, 24, 32, 32, the elements being generally analogous in their atomicity and in other chemical characters."

I have no desire to discuss Mr. Wilde's ingenious speculations, whether in his paper of 1875 or that of 1894; and, as far as the position of helium is concerned, it would seem desirable to wait for further light on its nature.—I am, &c.,

J. H. GLADSTONE.

17, Pembroke Square,
November 17, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxi., No. 22, November 25, 1895.

M. Launelongue has been elected a Member of the Section of Medicine and Surgery, *vis* the late M. Verneuil.

On Para-ethoxyquinoline. — C. Grimaux. — The author describes the preparation and properties of quinethol, $C_{11}H_{11}NO$, its hydrochlorate, sulphates, and nitrate. Quinethol is a weak base; its salts with the organic acids are dissociated by water. By dissolving quinethol in sulphuric acid and adding two mols. of fuming nitric acid we obtain nitroquinethol, $C_{11}H_{10}(NO_2)NO$. It has feeble basic properties. Amidoquinethol, $C_{11}H_{10}(NH_2)NO$, is obtained by reducing the nitro-compound with stannous chloride in a hydrochloric solution at a temperature below 50° . It is easily diazotised, and yields tinctorial diazo-compounds. Quinethol has no action upon intermittent fevers, and has no anti-periodic properties.

Rapid Determination of Nitric Nitrogen in Vegetable Substances.—P. Pichard.—This paper will be inserted in full.

Action of Phenol upon Mercurous Iodide.—Maurice François.—At the temperature of ebullition the decomposition of mercurous iodide by phenol is limited by the quantity of mercuric iodide existing in solution. The decomposition always ceases when 100 parts of liquid contain 2.75 grms. mercuric iodide. In presence of metallic mercury if a solution of mercuric iodide in phenol contains more than 2.75 grms. of mercuric iodide in 100 grms. of solution, there is found mercurous iodide.

Manganese Silicide.—M. Vigoureux.—Manganese silicide has a metallic lustre, and is very hard, brittle, and perfectly crystalline. Its specific gravity at 15° is 6.6. It is unalterable in air and fusible in the reverberatory furnace. Fluorine attacks it at the ordinary temperature, forming white fumes of silicon fluoride. If heat is applied there ensues combustion, with flame and incandescence. Dry chlorine acts at 500° with lively incandescence, silicon chloride being evolved. Iodine and bromine react less readily. Caustic potassa with the aid of heat attacks this compound energetically. Its composition is $SiMn_2$.

Toxicity of Acetylene.—L. Brociner.—Acetylene exerts merely a very feeble poisonous action, not more marked than that of the ordinary hydrogen carbides, such as formene, ethylene, or propylene. Animals exposed to the action of mixtures containing considerable proportions of acetylene for several hours do not succumb if we are careful to operate in presence of a considerable quantity of oxygen, and to renew the gaseous mixture so as to prevent the products of the animal's respiration from accumulating.

Some Reactions of Tartaric Acid and the Alkaline Tartrates.—L. Magnier de la Source.—If to a concentrated solution of potassium acetate we add a relatively small proportion of tartaric acid (though more than suf-

ficient to precipitate with an equal volume of solution of potassium sulphate) there is no immediate precipitate. The addition of a mixture of ether and alcohol renders the precipitation more rapid, and the addition of acetic acid renders it immediate.

Presence of Laccase in Fungi.—Em. Bourquelot and G. Bertrand.—Laccase exists not merely in green plants, but in such as are devoid of chlorophyll.

Distribution of the Nitrogenous and Mineral Substances in Bread.—There exists no more nitrogenous and saline matter in the crust of bread than in the crumb if both are brought to the same degree of dehydration. The baking of bread does not effect any destruction of matter. There is a loss of fatty substances and an increase of saccharine matter, but the total weight does not vary to an appreciable extent. Dry bread does not contain more nutritive matter than the dry flour used in its production.

MISCELLANEOUS.

Corrugated Packing Paper and Boards.—We have received, from Messrs. Bracht and Friedlaender, specimens of an improved packing material which they are introducing to the English market. From a careful examination we think that its use will be found very convenient and safe for packing breakable goods, as well as for forwarding samples for analysis, specimens of dry colours and other fine chemicals, *etc.* The double corrugated paper is calculated to supersede other materials as an enclosure for phials, specimen tubes, and glasses, as it combines lightness with great resistance to pressure and concussion. It is manufactured in a variety of colours and shapes adapted for various purposes.

NOTES AND QUERIES.

Glass Cloth for Acid Filtering.—Will some reader kindly state where the article known as glass cloth for acid filtering purposes can be obtained, and who are the manufacturers?—W.

TO CORRESPONDENTS.

H. F. J.—We are of course aware of the two views you mention concerning the electrodes in voltaic cells; but we cannot trace who is originally responsible for each opinion.

ACETONE—Answering all requirements.

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THE CHEMICAL NEWS.

VOL. LXXII., No. 1883.

INVESTIGATIONS OF THE CHEMICAL HISTORY OF THE BARLEY PLANT.*

By C. F. CROSS and CLAUD SMITH.

It is becoming evident that useful research in matters agricultural must henceforth take the form of physiological diagnosis. The investigation of crops in relation to soils and fertilisers has of course rendered incalculable service, and in this country the distinguished group who have presided over the Rothamstead Experimental Station have done much to lay the foundation of sound scientific practice. At this date, however, we have to confess that the fundamental problem of *Assimilation* is, so far as the agriculturist is concerned, so much "virgin soil." While experience and the vast accumulation of observations furnish more or less accurate impressions of the results of the process, the process itself is one of those factors of production which are still "taken for granted." We may except, perhaps, from this general statement certain positive results which have followed the application of methods of selection based upon observation of variations of particular products of assimilation, such as the improvement of the sugar beet in relation to the production of sugar. But even here the methods pursued are empirical and involve no consideration of the actual mechanism of assimilation.

Now that methods of more exact proximate resolution of mixtures of carbohydrates are in our hands, the time has arrived for their application to growing crops as the necessary basis of a knowledge of the course of assimila-

tion, or more generally of the chemical life history of the plant. It would be out of place to prejudice the enquiry by asking what are the useful results likely to follow from such investigations. It must be positively assumed that such results will certainly issue, and the work must be begun upon the conviction.

On this view we have carried out for two years periodical investigation of barley crops growing upon the experimental plots of the Royal Agricultural Society at Woburn. We selected two plots giving respectively the minimum and maximum yields of grain over a succession of years, viz.—

Plot 1. Permanently unmanured.

Plot 6. Manured with 200 lbs. sulphate of potash, 100 lbs. sulphate of soda, 100 lbs. sulphate of magnesia, 3½ cwt. superphosphate of lime, and 275 lbs. nitrate of soda.

Our observations have been chiefly directed to the cellulosic basis of the straw. It has been previously shown that the celluloses of cereals are widely differentiated from the normal type in the presence of a large proportion of furlural yielding constituents. While there are in part pentoses or pentosan groups, they consist in the main of oxidised derivatives of the hexoses; and being the most characteristic constituents of the permanent tissue it was clearly necessary to study the history of their assimilation as the basis of a systematic investigation of the history of the plant.

We now give without further preliminary explanation the actual experimental numbers arrived at, as the scope of the investigation will be grasped from a mere inspection of the tables of figures.

In reference to the methods of observation, the results of which are embodied in the table, it is perhaps necessary to explain what is meant by "permanent tissue." The plant may be regarded as made up of cellular and fibrous tissue, cell contents, and excreted products. To eliminate the latter and isolate the tissue the following process has been employed:—

1. After reducing the plant to "chaff," exhaustive extraction with boiling alcohol. 2. The residue is digested

* Read before the British Association (Section B), Ipswich Meeting, 1895.

BARLEY SAMPLES.—WOBURN.

Date.	Age of Crop.	Plot 1.—Minimum Yield.			Plot 6.—Maximum Yield.			Ratio.
		Plot.	Total Dry Matter. Per cent.	Furfural. (a) Per cent of dry weight.	Permanent Tissue. P.c. of dry weight.	Furfural from Permanent Tissue. (b) P.c. on tissue.	Tissue. (c) P.c. on total.	
1894.	May 7. 6 weeks	1	19.4	7.0	53.4	12.7	6.8	1.03 : 1
		6	14.7	7.0	55.9	10.3	5.7	1.23 : 1
	June 4. 10 weeks	1	17.6	7.7	52.9	11.6	6.1	1.26 : 1
		6	13.5	8.1	58.5	13.4	7.8	1.04 : 1
	July 10. 15 weeks	1	42.0	9.0	65.7	9.8	6.4	1.40 : 1
		6	32.9	10.6	65.7	12.5	8.2	1.30 : 1
	Aug. 21. 21 weeks	1	64.0	11.9	70.0	14.5	10.1	1.18 : 1
		6	64.6	13.4	70.5	15.0	10.6	1.26 : 1
	Aug. 31. 22 weeks 3 days	1	84.0	12.7	75.0	16.5	12.4	1.02 : 1
		6	86.4	12.4	78.4	15.1	11.8	1.05 : 1
1895.	May 15. 7 weeks	1	20.6	6.6	53.9	10.2	5.5	1.20 : 1
		6	17.8	5.8	56.7	9.6	5.4	1.07 : 1
	June 18. 12 weeks	1	34.6	8.0	38.2	14.7	5.6	1.42 : 1
		6	33.4	7.6	44.5	15.0	6.7	1.14 : 1
	July 16. 16 weeks	1	52.8	12.1	55.6	16.3	9.1	1.33 : 1
		6	54.4	10.6	46.2	19.1	8.8	1.20 : 1
	Aug. 16. 20 weeks	1	66.8	9.2	49.1	17.0	8.3	1.10 : 1
		6	65.0	9.8	49.8	19.1	9.4	1.04 : 1
	Sept. 3. 22 weeks 4 days	1	84.8	10.4	45.7	17.6	8.0	1.31 : 1
		6	86.3	10.2	45.3	17.3	7.8	1.30 : 1

NOTE.—The experimental results are expressed throughout upon the *whole plant*. For the agricultural bearings of the numbers it is necessary to further analyse the later numbers in reference to grain and straw. These points will be dealt with elsewhere. Our scheme of experiments for 1896 includes an examination into the effects of preventing the formation of seed upon the permanent tissue of the stem.

four hours at the ordinary temperature with dilute caustic soda (20 per cent NaOH) and then washed, at first with cold, lastly with boiling water. 3. The residue is then digested with dilute hydrochloric acid (2 per cent HCl) in the cold, and then washed with cold, lastly with boiling water.

The residue we take as approximately representing the tissue constituents. The process being one of hydrolysis is of empirical and somewhat arbitrary value. The value of the results will be estimated by their own internal evidence. If the definition "permanent tissue" be objected to, it is easy to substitute the more correct description, which is "the residue from treatments by chlorophyll solvents and by hydrolytic agents, alkaline and acid, under carefully regulated conditions." The product has served the purposes of these investigations, and will, we think, be seen to have the value of a "constant."

We draw a number of conclusions from the result:—

1. The conditions of soil nutrition are seen to have very little influence upon the composition of the plant. Comparison of the numbers for the two plots taken in pairs show certain fluctuations, it is true, and these are most marked at the most active period of growth, *i.e.*, at the flowering stage. Contrasted with this, the final condition of the tissue, *i.e.*, at maturation, may be taken as identical under conditions of minimum and maximum soil nutrition, as it may also at the initial stages of germination and early growth. The plant, in other words, is, as regards soil nutrition, constant or invariable in respect of the relation of its products of assimilation.

2. If we had had the selection of extreme variations of season we could not have chosen better than as between 1894 and 1895. The influence upon the experimental numbers is extreme, more especially in regard to "permanent tissue." In the comparatively wet season of 1894 there is a steady increase of permanent tissue; in 1895 the brilliant and continuous sunshine of the period up to and including that of flowering determined a totally different course. The proportion of easily hydrolysable carbohydrates shows a steady increase during the maturation period at the expense of permanent tissue. The total dry matter, on the other hand, was influenced only in the stages up to and somewhat after the flowering period. Dehydration was for obvious reasons much more active in 1895, and the difference of condition in this respect in the case of plot 6 is quite remarkable. Certain industrial consequences follow from the history of the tissues (see foot-note to table): (1) the feeding value of straws grown in dry seasons is high: and (2), conversely, the paper-making value of such straws is low. Moreover, while we may well assume a diminishing feeding value of the 1894 straw during the period of maturation, it would appear that in 1895 there is an actual increase of feeding value of the mature straw over the straw taken at the flowering period. It is of course to be admitted that artificial hydrolysis is only a crude measure of digestibility, and it would be important to confirm the conclusion by actual feeding experiments. That must be deferred to future opportunities.

3. The fufuroids have been diagnosed in various ways, chiefly with the view of determining their distribution as between hydrolysable and non-hydrolysable (permanent tissue) constituents. In the early and late periods of growth the fufuroids are in the main of cellulose character. The greatest divergence is seen to occur at the most active period of growth, and here there is an accumulation of easily hydrolysable fufuroids. The maximum proportion was similar in the two seasons; in both crops there is a gradual rise to and falling from the maximum; in the 1895 crop there was a marked change after cutting, and the change in the character of the fufuroids was accompanied by a retrograde change in the "permanent tissue." This retrograde movement, it will be noted, was continuous from the flowering period and in exact contrast to the history of assimilation in 1894.

A fair interpretation of the results appears to be this:

the fufuroids are by no means excreted products, but available for assimilation, and they are in fact continuously assimilated to permanent tissue (cellulose). Owing to the deficient moisture in the period to July 16th the building up of new matter (growth) was interfered with, and the "permanent tissue" was put under contribution for nutrient material which, under ordinary conditions, would have been drawn from *cell-contents* and not from tissue.

In the month July 16th to August 16th there is, in fact, a notable falling off in the total quantity (proportion) of fufuroids, which confirms the view that these constituents were put under contribution selectively, to the general needs of the plant.

Viewed broadly and generally these investigations show how very different are the results of physiological study of the history of crops from those of investigations of soil nutrition. The essential characteristics of the plant are maintained independently of the factors of soil nutrition. The comparative study of the two crops proves this conclusively.

In our opinion systematic investigation of the actual physiological, *i.e.*, chemical, constants of the plant, will lead to results of which at present it is impossible to predict the import.

Take it that we had been able to make a complete proximate resolution of the straw substance from time to time, instead of confining ourselves to one group of the carbohydrate constituents: it is easy to see that much wider and more positive conclusions could have been drawn.

But private enterprise has its obvious limits, and exhaustive investigations of this character can only be undertaken by institutions fully equipped and supported by adequate funds.

We hope this preliminary contribution will serve as an indication of the results likely to follow from the systematic work of such an institution.

ON THE PERCENTAGE OF ARGON IN ATMOSPHERIC AND IN RESPIRED AIR.*

By ALEXANDER KELLAS, B.Sc.,
Assistant in the Chemical Department of University
College, London.

ALTHOUGH blood invariably contains a small amount of dissolved nitrogen, it appears that with animals no absorption of that gas takes place than what is due to its solubility in the serum of the blood. Nor is nitrogen eliminated from the system in the elementary state.

At Professor Ramsay's suggestion, experiments have been made on the comparative amount of argon in ordinary air, and in air which had been frequently breathed, with the view of ascertaining whether, if the proportion of oxygen and carbon dioxide in air be very much altered, argon would either enter into, or be expelled from the respiratory system. The result of the experiments to be described is to show that the proportion of argon to nitrogen remains nearly normal, even when the air has been greatly altered in composition by respiration.

1. *Percentage of Argon in Atmospheric Air.*—A mercury reservoir, the capacity of which was accurately determined by weighing with water, held 555.2 c.c. The upper end was fitted with a three-way tap, sealed on to the glass. Through this tap was admitted air, purified by passage over soda-lime and phosphoric anhydride, to remove water-vapour and carbonic anhydride. This reservoir was jacketed with water of known temperature, so that the volume of the air could be measured with great exactness. The other branch of the three-way tap led to a tube filled with copper, in order to absorb oxygen; one

* A Paper read before the Royal Society.

containing copper oxide to destroy any organic matter which might have been present, and one filled with magnesium turnings to absorb nitrogen; these tubes were kept red hot. Other tubes were filled with soda-lime and phosphoric anhydride, so as to remove water and carbon dioxide, which might have been produced. The air was circulated over these absorbents until little but argon was left. The gas-holder was filled three times at 18°8' C., and 752·1 m.m. pressure. After absorption had nearly ceased, the remaining gas was pumped out of the tubes, mixed with oxygen, and sparked for many hours in presence of caustic soda, to remove the last traces of nitrogen. The residue, after absorption of oxygen with potassium pyrogallate, measured 15·91 c.c. at 21°4' C., and 754·5 m.m. pressure.

Reducing both volumes to standard temperature and pressure, it appears that—

1542·0 c.c. of air yielded 14·45 c.c. of argon, or
100·0 c.c. of air contain 0·937 c.c. of argon.

Calculating the percentage in atmospheric nitrogen, we have—

100 c.c. of mixed atmospheric nitrogen and argon contain 1·186 c.c.

Owing to the avoidance of the presence of water during these experiments, they are probably more accurate than the original experiments of Lord Rayleigh and Professor Ramsay. They found ("Argon," *Phil. Trans.*, 1895, A, pp. 221 and 214) 1·04 and 1·03 in two experiments in which the nitrogen was removed by sparking with oxygen in presence of dilute caustic soda; and 1·11 when the nitrogen was removed by means of magnesium.

Owing to the vacation, it has not been possible to put this result on record before now. And Th. Schloësing, jun., has recently published *Comptes Rendus*, vol. cxxi., p. 605) the results of a series of estimations in which the percentage of argon in atmospheric nitrogen was found to be 1·180 to 1·185, or as a mean 1·183 per cent, a number almost identical with that just recorded. M. Schloësing has re-calculated the ratio which ought to subsist between the densities of atmospheric and "chemical" nitrogen on the basis of his determinations; but in doing so, he has made use of the value 1·2505 grm. as the weight of one litre of the latter, instead of 1·2511 (*Phil. Trans.*, 1895, A, p. 189). Moreover, he has assumed Regnault's value, now superseded, for the weight of 1 litre of hydrogen, viz., 0·0896 grm., instead of that given by the more recent determinations, 0·0899 (*Phil. Trans.*, 1895, A, p. 292). These are not serious errors, but it is more satisfactory to calculate the correct number. The question is:—If the weight of a litre of pure nitrogen is 1·2511 grm., and of argon 1·7818 grm., and if atmospheric nitrogen contain 1·185 per cent of argon, what should be the weight of a litre of the latter? The answer is 1·2574. Lord Rayleigh found the number 1·2572, one almost exactly identical.

For material for the second part of this research, I have to express my thanks to Dr. Marcet, F.R.S., and his assistant, Mr. Floris. The air was analysed before having been breathed, and had the normal composition:—

Nitrogen and argon..	..	79·02	per cent
Oxygen	..	20·93	"
Carbon dioxide..	..	0·05	"

100·00

The air was breathed over and over again by Mr. Floris, until after ten minutes' respiration its composition had become:—

Nitrogen and argon..	..	80·96	per cent
Oxygen	..	5·40	"
Carbon dioxide..	..	13·64	"

100·00

An estimation of the argon was carried out in precisely the same manner as before, on 1297·8 c.c. of breathed air,

measured at 17°2' C. and 759 m.m. pressure. But the air was breathed over water, the requisite change of volume on respiration having been secured by breathing into one of Dr. Marcet's counterpoised gas-holders. The argon found measured at 17°7' C. and 752·3 m.m. pressure 12·85 c.c. These numbers corrected give—

1196 c.c. of breathed air yielded	11·72	c.c. of argon.
100 c.c. " "	0·980	c.c. of argon.

Calculating the percentage on the nitrogen, we have:—

100 c.c. of nitrogen and argon of breathed air contains 1·210 c.c.

This percentage is larger than that in normal air. One of two suppositions may be made:—Either the increased amount is due to the air having been confined over water during breathing, or argon is given off from blood in greater amount than it is absorbed, when the composition of the air in the lungs is so much altered; the former appears the more probable supposition. In any case the difference is not great; and it would appear that argon, like free nitrogen, plays no important part in the animal economy, save as a diluent.

ON THE ORIGIN OF THE ARGON AND THE HELIUM IN THE GASES ESCAPING FROM CERTAIN SULPHUROUS SPRINGS.

By L. TROOST and L. OUVARD.

In his communication concerning the presence of argon and helium in the gases liberated from the sulphurous springs of Cauterets, Dr. Bouchard has indicated the importance of examining, from the same point of view, the gases in solution in waters which flow or stand on the surface of the ground.

We might, in fact, put forward the idea that the gases liberated by the sulphur waters are derived exclusively from the atmosphere. The solubility of argon might cause us to admit that the gases carried down by the waters from the surface into the depths of the earth, re-ascend with the same waters which have been rendered alkaline by a sulphide.

To throw a light on this question we have examined the gases from the water of the Seine (supplying the laboratories of the Sorbonne), and from sea-water, collected at high tide on the shore of the ocean. We have there sought for helium, independently of argon, which we were certain to find, since it is more soluble than nitrogen, which always exists in waters in contact with the atmosphere.

These gases, collected with the ordinary precautions and freed from carbonic acid by means of potassa, were treated in two different manners. The nitrogen was removed either by causing it to be absorbed by magnesium heated to redness, or by combining it with oxygen under the influence of electric sparks in presence of potassa.

This latter procedure is more tedious but more trustworthy, since the gas, constantly enclosed in the same glass tube over mercury, and without any transferences, is preserved from any mixture, even with very minute quantities of atmospheric air.

The gaseous residue obtained was dried over melted potassa and placed in connection, as in our former experiments (*Comptes Rendus*, cxxi., p. 394), with a Plücker tube with electrodes of magnesium in which a vacuum had been made by means of the mercurial pump.

The tube was repeatedly swept out with the gases in question, the vacuum being made each time anew. Then, after a final introduction of the gases, the effluve was caused to pass between the magnesium electrodes.

The spectroscope from the first constantly indicated the presence of traces of nitrogen, but on prolonging the experiment they disappeared. We were then able to decide that the spectra furnished by the gases from the wells of Cauterets were strikingly different from those afforded by the gases extracted from the water of the Seine and from sea-water.

These latter give the spectrum of argon, and merely traces of the spectrum of helium scarcely perceptible and often doubtful, whilst the gases collected at the well-head of the Baillière, or extracted by boiling the water from the same spring, give very distinctly the characteristic rays of argon and those of helium, and that the gases collected at the well-heads of the sources of the Bois give especially the characteristic rays of helium.

The helium contained in the gases liberated from the mineral springs of Cauterets does not consequently seem to us to be due to the atmosphere. The gas is derived probably from the rocks in the strata which these mineral waters have traversed.

The presence of helium lately proved in a certain number of minerals, such as clèveite, bröggerite, orangite, monazite, &c., renders this conclusion at least possible, so that, outside of any medical consideration, the study of the gases evolved by mineral waters would derive an especial interest from the fact that these gases may supply us with new information concerning the elements of the rocks which these waters encounter in the strata whence they issue.

With reference to the above communication, Dr. Bouchard added the following observations:—

I have stated in the paper to which M. Troost refers that, in all probability, the therapeutic activity of the mineral waters in which I showed the presence of argon and helium is not due to these gases. I added, that if these gases were present in the waters which flow or stand on the surface of the earth, the question would be decided, since these (surface) waters have not the therapeutic value of the mineral springs in question. But if argon and helium are inert, it may not be the same with mineral substances with which they are in combination.

It is established, by the communication of M. Troost, that helium at least is derived from the depths of the waters. Among the mineral compounds of helium there may be some which, even in minimal cases, may exert a physiological action upon the organism. On this hypothesis the effect would be due not to helium, but to the metal with which it was combined, always supposing that such a compound or its derivatives were sufficiently soluble.—*Comptes Rendus*, cxxi., p. 798.

ON THE PRESENCE OF ARGON AND OF HELIUM IN A SOURCE OF NATURAL NITROGEN.

By CH. MOUREU.

QUITE recently M. Bouchard has pointed out the presence of helium in the gases of the springs of Bois (Cauterets), and that of helium and argon in the gases of the Raillière. Whilst studying the same subject, MM. Troost and Ouvrard have discovered an important property of argon and helium—that of being absorbed by magnesium at a very high temperature.

I have just recognised the same two elements together in another natural gas which escapes abundantly in large bubbles from the spring of Maizières (Côte d'Or). The water of Maizières is a lithium water containing a little calcium sulphate, and it has at the source the temperature of +12°. Thanks to the courtesy of M. Communaux, the director of the company, I have had at my disposal several litres of the gas. The specimens had been collected with all the usual precautions, so as to avoid con-

tact with air, which would necessarily have introduced argon.

The analysis over mercury showed me at once that the gas contained a small proportion of oxygen (about 2 per cent), the residue presenting all the negative characters of nitrogen.

To detect argon and helium I had recourse to the kindness of M. Deslandres, who has kindly undertaken these delicate experiments. After absorbing the nitrogen by lithium at a dull red heat, the gaseous residue was introduced into Plücker tubes at a low pressure, and, on being submitted to the effluve, it gave the characteristic rays of argon and of helium.

We may add that the proportion of these gases has been found rather considerable; the volume of the gaseous residue not absorbed by lithium is between one-tenth and one-fifteenth of the total volume.

Although the analysis has not been carried further, it seemed to me interesting to communicate these results to the Academy, not only on account of the presence of argon and of helium in a source of natural gas, but because of the relatively high proportion of these two elements in the gaseous mixture.—*Comptes Rendus*, cxxi., p. 819.

THE MANUFACTURE AND COMMERCIAL SEPARATION OF GLUCINUM.

By H. N. WARREN, Research Analyst.

PROBABLY one of the most eccentric metallurgical orders of the times has been recently executed at the Research Laboratory, in the method of manufacturing glucinum for jewellery purposes. In order to ensure a large percentage of glucinum in the ore selected, six pounds of emerald-dust and stones of dull water were specially imported from various parts of the world; ground to a fine powder, and the finer qualities separated by lixiviation and re-grinding. The powder so prepared was next thoroughly incorporated with four times its weight of sodic carbonate, and finally fused for three hours at the highest temperature of a powerful blast-furnace, and afterwards cast into square plates for further treatment. The second operation consisted in dissolving the melt thus formed as near as possible by the aid of supersaturated steam; and further effecting a complete decomposition by the introduction of an excess of hydrochloric acid, and evaporating it to dryness in order to render insoluble the silica present.

The siliceous residue having been washed and squeezed in a suitable press, was now rejected; the washings, together with the filtrate, being rendered alkaline by means of an excess of sodium carbonate, the solution having previously been freed from iron and chromium by acetates, in accordance with the usual separation of these metals.

The precipitate obtained by the introduction of the sodium carbonate was now thrown into a commodious glass receptacle, and heated with an excess of gaseous sulphurous acid, in which both the alumina and glucina dissolve. The solution thus obtained, upon being raised to ebullition, precipitates the alumina in a granular form, in place of the tedious gelatinous deposit obtained by the old ammonia process, which in the former case is washed with the greatest of ease. To the second filtrate thus obtained was added an excess of ammonium carbonate, and the solution well boiled; the glucinum carbonate being thus completely precipitated, also in a granular form, and admitting of being readily washed. The precipitate thus obtained being further intimately mixed with an excess of lamp-black and ignited out of contact with the atmosphere, the mass thus obtained being afterwards converted into bromide by adding upon it with bromine-vapour at a full red heat in clay retorts. The bromide distils over, and is readily reduced to the metallic form

by decomposing the same with an electric current of 12 volts 8 amperes.

The metal thus obtained, having been worked into articles, is now in the possession of the Ameer of Afghanistan.

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CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 304).

Preparation of Perchlorate of Potassium.

THE chlorate of potassium, the preparation of which I have described above, is used for the preparation of pure perchlorate and chloride of potassium.

As I said above, my object was to decompose the chlorate in such a way as to make on, the one hand, the greatest possible quantity of perchlorate, and on the other hand, a quantity of perchlorate just sufficient to make the chloride required to estimate its molecular relation to silver.

M. Marignac has published in his works the methods of obtaining this result, and to them I have nothing to add. I will confine myself to saying that I effected the reduction of chlorate into perchlorate and chloride in a large platinum retort, *the inside of which was first polished*, the neck on the lid of which entered into a large tube 50 c.m. long, containing a roll of asbestos packing, as I shall describe further on in a special memorandum.

The retort rested on an earthenware tripod, which was strengthened by iron wires; it was heated by means of a single Bunsen flame through two pieces of wire gauze, to distribute the heat evenly, which is *indispensable*.

I reduced it in four operations; two being for the purpose of getting from about 50 to 60 per cent of perchlorate of potassium, and two for getting 10 per cent only of this salt, entirely decomposing the chlorate experimented on.

The first operation was done at the lowest possible temperature, and occupied as much as twenty-six hours. I found that by keeping the fused chlorate at the temperature at which oxygen is slowly disengaged, and the vessel makes a noise or decrepitation similar to that heard when fresh water is heated beyond 80° in a metallic vessel, dissociation took place with an evolution of heat; the fused mass was eventually agitated, and finally became pasty. When it reached this state, all the chlorate was destroyed, and the maximum of perchlorate was obtained. The separation was effected without liberating a trace of chlorine, but the oxygen disengaged smelt of *ozone*. If, during the dissociation, which is exothermic, one does not sufficiently reduce the supply of heat, the mass heats itself until the platinum vessel becomes incandescent, as I have often found when reducing chlorate in a covered platinum crucible. In this case, not only does the chlorate decompose without forming perchlorate, but the greater part of the salt already formed decomposes, and leaves chloride only. This decomposition is, therefore, slightly explosive, and may, if one does not take care, cause the loss of part of the salt submitted to the action of heat. Whether the separation be made *slowly or quickly*, the chloride and perchlorate formed are white; there is no evolution of free chlorine, the chloride is neutral to litmus paper, and the platinum vessel is not altered at all.

I took the greatest pains to satisfy myself of these facts, as mentioned in the special memorandum on this subject, because, during my previous work, when working on siliceous chlorate, I always noticed a sensible evolution of chlorine, a very slight attack on the platinum, and the presence of this metal in the form of chloroplatinate in the chloride made.

I then turned my attention to obtaining the greatest possible quantity of perchlorate.

In two operations successfully carried on for this purpose, I warmed the chlorate to a temperature just sufficient to induce a *very weak* evolution of oxygen, and I kept the temperature constant from 8 a.m. to 6 p.m. for *two days and a half* consecutively, the length of time necessary to reduce the mass to a pasty condition, and obtain at the constant temperature the cessation of the evolution of oxygen, and the absence of very light fumes in the large long tube into which the neck of the retort lid entered.

To procure the perchlorate necessary for producing the amount of chloride required for estimating its molecular relation to silver, I noted the time required for the total decomposition, *at the lowest possible constant temperature*, of the perchlorate, effected by working on a mixture of almost equal weights of chloride and this salt, made from about 100 grms. of chlorate.

After oxygen ceased to be evolved at constant temperature—which is coincident with the complete dissociation of the chlorate, and the formation of the greatest amount of perchlorate compatible with this reaction—I gently raised the temperature until I caused once more a slight evolution of oxygen, and the appearance of the saline fume; I then kept the temperature constant for six hours. I found, by a preliminary trial, that at least twelve hours were required to decompose the whole of the perchlorate in the mixture at this temperature.

Separation of Perchlorate and Chloride of Potassium.

I effected this separation by dissolving the salt in pure cold water and using then just enough water to make a saturated chloride solution. Directly the chloride was dissolved, which was done in enclosed and purified air, the liquor coloured a Bunsen flame blue, though a *very much lighter* tint than chlorate gives. The solution was drawn off each time, and, although quite clear, it was poured into a filter-paper which had been most carefully washed with dilute hydrofluoric and hydrochloric acids and pure water, arranged in a platinum funnel covered by a bell-jar, the surface of which, as well as the glass plate on which it stood, was wetted. The solution was evaporated nearly to dryness in a loosely covered platinum dish, under a bell-jar filled with air saturated with moisture, so as to prevent, *as far as possible*, the saturated solution from rising up to the edge of the dish and depositing solid chloride on it.

The mother-liquor from chloride, crystallised by cooling, was *neutral* to litmus paper; it was drawn off into a platinum dish, and again evaporated down to saturation point under a damp bell-jar. The chloride deposited by cooling was separated from the mother-liquor, and this was evaporated to dryness under a damp bell-jar, carefully separating the chloride on the edge of the dish. By working thus, I obtained, in decreasing quantities, three samples of chloride made at the same time as the perchlorate.

I have most carefully examined the spectrum of each of these three samples, and found them to be identical.

I used the second sample to find out what residue it contained, and found none.

I shall describe further on how I treated each of these chlorides when estimating their molecular relation to pure silver.

Without removing the crystalline powdered perchlorate from the retort, I crystallised it three times, changing the mother-liquor and the water with which it was partially washed each time; they yielded a salt which coloured a hydrogen flame *pale* blue, and gave a potassium spectrum without the sodium line, similar to that of the chloride made at the same time as the perchlorate.

The boiling perchlorate solution, when put into a Bunsen flame on the end of a fine platinum wire spiral, coloured it a very pale blue. *Spectrum analysis did not show the sodium line*. This experiment was repeated

several times—whenever the state of the air allowed it—and always with the same result.

I have plunged into this boiling perchlorate solution several fine platinum wire spirals, coated with spongy platinum, previously heated to redness. I have left them under a large bell-jar filled with the air of the room where I was working, for the purpose of showing to several people that pure perchlorate coloured a flame blue and had no sodium line in its spectrum. I found that after from twenty-five to thirty minutes the crystallised perchlorate on the platinum spiral had absorbed enough sodium from the air to show the sodium line, very faintly it is true, but still unmistakably. In fact, from the moment I left the spirals under the bell-jar, the air of the room, which took the place of the air in the bell-jar by diffusion, became charged with sodium owing to the draughts in the room. One must be well acquainted with all the difficulties met with in a research of this nature in order to get a true idea of them. I express myself more fully on this subject in my "Study of Atmospheric Air," to which I beg to refer my readers.

The perchlorate of potassium which had been crystallised three separate times in a platinum retort covered by its domed top, and filled with enclosed and purified air, was reduced to chloride in it. This decomposition, when carefully done, is not difficult; *the separation into chloride and oxygen was effected without evolving any chlorine, and the chloride was neutral to litmus paper.*

I treated the chloride made from perchlorate in exactly the same way as chloride made at the same time as this salt; that is to say, I put it into just sufficient cold water to dissolve it. The solution was passed through carefully cleansed filter-papers without leaving any residue after the filter was washed. The clear liquid was evaporated to saturation at 100°, in a platinum dish loosely covered with a sheet of the same metal, and under a damp bell-jar. The mother-liquor, when poured off from the crystallised chloride, was in its turn evaporated to saturation at 100°; and, finally, this last mother-liquor was dried in a loosely covered platinum dish under a damp bell-jar.

I have thus obtained three samples of chloride made from perchlorate under conditions which yielded by dissociation of chlorate, on the one hand, the greatest possible amount of this salt and the least possible of chloride; and on the other hand, one-sixth part, at the most, of perchlorate, and the rest chloride.

The second sample of chloride made from perchlorate was used for showing the spectrum of the metal in it. I found the spectrum to be identical with that of chloride made at the same time as the perchlorate.

Lastly, I have worked on three samples, in decreasing quantities, of chloride made by crystallisation during the course of an experiment undertaken for the purpose of studying the conditions to be fulfilled in order to *partly* decompose the perchlorate formed by the complete dissociation of the chlorate.

All these chlorides, when dissolved in water, gave *clear* solutions, *neutral* to litmus paper; nevertheless, when heated in a platinum dish with pure chloride of ammonium, *with an acid reaction*, to a sufficiently high temperature to evolve white fumes, they gave off vapour which turned red litmus paper distinctly blue.

Fearing that traces of sulphate of potassium were present in these chlorides, I submitted them all to special treatment.

Treatment of Chloride of Potassium by Pure Chloride of Ammonium.

All the samples of chloride of potassium mentioned above were melted in pure sal-ammoniac, which was prepared by passing ammonia and hydrochloric acid gases through pure water in a large platinum apparatus, supplying always an *excess* of ammonia. The gases were brought through purified rubber tubes, weighted with platinum to keep the open end down.

The solution, which smelt strongly of ammonia, was

evaporated to saturation in the platinum apparatus. After cooling it quickly, the mother-liquor was poured off and entirely changed.

The chloride of ammonium left in the apparatus gave no *sodic reaction*—a proof that, under the above-mentioned conditions, neither the ammonia nor hydrochloric acid gas brought any trace of sodium. I emphasize this point, because the use of this sal-ammoniac to reduce oxides free from sodium into chlorides always forms compounds which give conclusive evidence of the presence of sodium *when these chlorides are hygroscopic*. I shall return to this subject when describing my researches on chloride of calcium.

Having found that sal-ammoniac, when separated, was quickly contaminated by sodium from the air, I sublimed part of it in a platinum retort in an *atmosphere of dry ammonia*. In order to do this, I put the platinum retort containing the salt to be sublimed on an iron plate in a gas-stove that I have described and illustrated on page 553 of my "New Researches on the Laws of Chemical Proportions," taking care to leave the *upper two-thirds* of the retort outside the stove, and to shield this part from the gases at the temperature of the volatilisation of sal-ammoniac, by means of a second iron plate.

Having ground the neck of the retort lid, as far as possible into a long tube, I passed a tube for the supply of dry ammonia, which was admitted through a cork at the other end of it, through it, as far as the entrance to the dome of the lid.

The air in the retort being entirely replaced by dry ammonia, I regulated the heat imparted to the gases by the combustion of coal-gas in the following manner, so as to sublime the sal-ammoniac slowly:—I put an open tube containing sal-ammoniac, with the upper end protruding from the stove, in the bottom of the retort, to act as a thermometer. When, by reason of the high temperature of the gas, I saw the sal-ammoniac crystallising *slowly* in rings on the upper part of the open tube, I kept the supply of coal-gas burning in the stove constant for five hours by means of a regulator. Five hours were actually required for slowly subliming about 150 grms. of sal-ammoniac, the quantity on which I was working.

I have gone into these minute details because I have been asked to do so by certain chemists who, having wished to obtain some sal-ammoniac sublimed in platinum, have failed to do so, though they followed the directions given on page 473 of my "New Researches on the Laws of Chemical Proportions."

Sal-ammoniac volatilised as I have just described, condenses in the same retort in the form of a *very thick, transparent, colourless, and elastic* ring, which becomes detached after cooling for some time, becoming entirely opaque. The domed top is filled with powdery sal-ammoniac, smelling strongly of ammonia, and rapidly taking up sodium from the air.

Sublimed chloride of ammonium gives no *sodic* characteristics to flames; but when kept under a bell-jar shielded from atmospheric dust, it slowly condenses sodium compounds on its surface, as all solids do under similar conditions.

Coming back to the treatment of chloride of potassium by chloride of ammonium.

To fuse chloride of potassium, I put in the bottom of a large platinum crucible, *quite free from iron*,* first of all a layer of alkaline chloride in powdered crystals, then a

* A crucible made of pure platinum is deprived of the iron introduced into it by welding, by treating it, at a low red heat, with chloride of ammonium. This treatment is continued until one gets a *colourless* button of melted chloride on fusing a mixture of pure alkaline chloride and sal-ammoniac. So long as the platinum retains traces of iron, an alkaline chloride melted in it with sal-ammoniac forms a red or pink mass, and loses the ferric oxide when dissolved in water. Alkaline chlorides dissolve ferric oxide when melted, and loose it when cooled. It is only necessary to dissolve melted ferri-ferrous chlorides in cold water to obtain, on filtering the solution and evaporating the liquid, a perfectly white saline mass, which one can melt in a pure platinum crucible with sal-ammoniac, and form, on solidification, an absolutely colourless button.

piece of sal-ammoniac, and finally I filled the crucible with melted chloride mixed with small pieces of sal-ammoniac.

After putting the lid on the crucible, I warmed it slowly to a dull red heat, then I kept it at least fifteen minutes at a *bright red heat*, until, on lifting the lid, the gas bubbles seen round the edge of a crucible containing an alkaline chloride melted with sal-ammoniac, had entirely disappeared. I quickly poured the chloride into a recently heated and cooled platinum dish. If the operation has been properly conducted—that is to say, if the chloride has been kept fused at a high temperature for a sufficient length of time—the button is *colourless, limpid, and transparent*, and contains no gas bubbles.

When I found bubbles present, a sign of the existence of sal-ammoniac or of the products of decomposition, I *re-melted the button* in a double crucible of pure platinum, and I then turned the melted chloride into a platinum dish.

The buttons, when cold, were broken in an agate mortar, and the pieces, the edges of which had become milky, were put into flasks with ground glass stoppers.

Since they were made from chlorates and perchlorates which left no trace of solid residue on volatilisation, I naturally dispensed with testing the chlorides afresh. The very great care that I took during the work to prevent siliceous and sodic atmospheric dust from falling into the salt is a sufficient guarantee for its purity.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 5th, 1895.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. John Allan, 242, Moss Lane East, Manchester; Herbert Lister Bowman, 13, Sheffield Gardens, Kensington, W.; James Kerry Burbridge, Moor's Lea, Winchmore Hill; Frank Dixon, 73, King Edward Road, South Hackney, N.E.; Joseph Edward Morrison, Montreal; Harold Rostron, 70, Davenport Street, Bolton; Peter B. Scotland, 30, Stirling Street, Airdrie, N.B.; Aitken Migget Simpson, 4, Kitto Road, St. Catherine's Park, S.E.; Henry G. Smith, Technological Museum, Sydney, N.S.W.

Mr. OTTO HEHNER called the attention of the Society to what he regarded as unprofessional conduct on the part of a Fellow of the Society whose name appeared on the certificates of certain candidates who were to be balloted for that evening.

Professor ARMSTRONG then moved, and Mr. GROVES seconded, that the Council be requested to consider this case. Professor TILDEN having spoken in support of the motion, it was put to the meeting and carried.

The following were duly elected Fellows of the Society:—George Percy Bailey, B.A., The Earl of Berkeley, Arthur Jenner Chapman, Wm. Chattaway, George Bertram Cockburn, B.A., Charles Crocker, Gurney Cuthbertson, William Dixon, Edward Henry Farr, Charles James Fauvel, Patrick Joseph D. Fielding, Jervis E. Foakes, Stanley Fox, James Gardner, Edward Graham, B.Sc., Edward Henry Grossmann, The Rev. Henry Arthur Hall, M.A., Edgar Septimus Hanes, C. E. Harrison, B.A., James Henderson, B.Sc., Thomas Hawkins, Percy Heriot, Frederick Arthur Hillard, B.A., Arthur Edward Holme, M.A. (Oxon.), Alfred James, Frederick Edward Johnson, William Oakes Kibble, Leonard P. Kinnicut, James McCreath, David James Morgan, William Henry Pennington, Martin Priest, W. T. B. Ridge, William

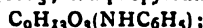
Round, William Augustus Rugginz, Clarence Arthur Seyler, B.Sc., Mathew Smith, B.A., Frank R. Stephens, George Stone, W. J. Tibbals, John Williams, B.A., Thomas Rowland Wingfield, and Harold E. Wright.

Of the following papers those marked * were read —

*141. "*Researches on the Terpenes. VI. Products of the Oxidation of Camphene: Camphoric Acid and its Derivatives.*" By J. E. MARSH and J. A. GARDNER.

In this paper some of the oxidation products of camphene are described, among them being camphoric acid, $C_{10}H_{14}O_6$, as chief product, camphoric acid in small quantity, terephthalic acid, and succinic acid.

From camphoric acid were obtained:—Anhydromcamphoric acid, $C_{10}H_{14}O_5$; cis- and trans-camphopyric acids, $C_9H_{14}O_4$; camphopyric chloride, $C_9H_{12}Cl_2O_2$; chlorocamphopyric chloride, $C_9H_{11}Cl_3O_2$; chlorocamphopyric anhydride, $C_9H_{11}ClO_3$; camphopyranilic acid,—



and salts of camphoric and camphopyric acids. With camphopyric acid is compared camphoric acid in respect of their both existing as cis- and trans-isomers, and also as regards the acid chloride, chloroacid chloride, and chloroanhydride, producible from both camphoric and camphopyric acids.

The reduction of camphopyric acid to hexahydrometaxylene has also been accomplished, while the constitution of camphene is discussed from the general analogy of camphoric and camphopyric acids, from the probability of their both containing a hexamethylene nucleus, from the fact of the production of both acids from camphene and from the probability that neither camphoric acid nor camphopyric acid is producible from camphoric acid.

DISCUSSION.

Professor ARMSTRONG inquired whether Mr. Marsh could give any further information as to the isomeric bromocamphor described by him on a previous occasion, since he (Professor Armstrong) had not been able to confirm Mr. Marsh's results.

If a molecular proportion of bromine be added to camphor heated on the water-bath, using 1 or 2 per cent in excess, so as to ensure the absence of camphor, an almost theoretical yield of bromocamphor (m. p. 76°) is obtained. If, to purify the product, it be dissolved in hot alcohol, the greater part of the bromocamphor at once crystallises out as the solution cools, and if the small amount of oily residue obtained from the mother-liquor—a mixture of mono- and dibromo-camphor—be digested with alcoholic potash, so as to reduce the dibromo-compound, this also is converted into well-crystallised bromocamphor.

According to Marsh (*Trans. Chem. Soc.*, 1890, 828), if camphor be brominated in presence of alcohol, almost half the product consists of an isomeric bromocamphor of ill-defined crystalline form and very low rotatory power. A product such as he describes can undoubtedly be obtained, but it is not difficult to separate bromocamphor from it, and its properties are certainly those of an impure material. It is desirable that this product should be more fully examined, and its nature definitely established, in view of the interest attaching to isomeric cis- and trans-modifications of camphor derivatives; the account given by Marsh is incomplete as it stands, and it is to be hoped that he will study further the action of bromine on camphor in presence of alcohol.

Mr. MARSH, in reply, said he had no doubt as to the existence of the second bromocamphor. He regarded the action of bromine on camphor as very considerably modified by the presence of alcohol, which, by reacting at once with the hydrobromic acid to form ethyl bromide, favoured the existence of the unstable isobromocamphor. The isobromocamphor has been obtained in crystals having a definite melting-point. Its specific rotation is more than 100° lower than that of the ordinary modification, while it is also lower than that of camphor itself. When distilled it is converted partially, without appreciable decom-

position, into the ordinary modification, the rotatory power after one distillation being raised about 50°, whilst ordinary bromocamphor may be readily obtained from the distilled product by crystallisation from alcohol.

*142. "New Derivatives from α -Dibromocamphor." By MARTIN O. FORSTER, Ph.D.

Early in this year a preliminary note was published in the *Proceedings* (p. 4), describing the behaviour of α -dibromocamphor towards nitric acid, an investigation undertaken at the suggestion of Professor Armstrong. It appears desirable to place on record the results which have since been obtained in this connection.

It has been already stated (*loc. cit.*) that a compound of the formula $C_{10}H_{12}Br_2O_2$ is produced when α -dibromocamphor is acted on by fuming nitric acid (*d. 1.52*), and that reduction with zinc dust and alcoholic ammonia converts this substance into a compound of the formula $C_{10}H_{13}BrO_2$. A fuller investigation has shown that the composition of these products is represented by the formulæ $C_{10}H_{14}Br_2O_2$ and $C_{10}H_{13}BrO_2$ respectively, which, in fact, correspond more closely to the analytical results already published than do the formulæ previously chosen.

The compounds $C_{10}H_{14}Br_2O_2$ and $C_{10}H_{13}BrO_2$ having given rise to numerous derivatives, it has been found necessary to adopt some system of nomenclature by means of which they may be designated, and the scheme which is now proposed has been selected because it aims at representing in the name of a derivative the class of compounds to which it belongs. It having been found that the initial compound $C_{10}H_{14}Br_2O_2$ has the properties of a lactone, this substance will be referred to as *dibromocampholid*; the product of its reduction, $C_{10}H_{13}BrO_2$, is an unsaturated (carboxylic) acid, and will be called *bromocamphorenic acid*, the termination "olid" being significant of lactones, whilst ethylenic linking is represented by the syllable "en."

Dibromocampholid, $C_{10}H_{14}Br_2O_2$, is obtained by the action of fuming nitric acid (*d. 1.52*) on α -dibromocamphor in quantity amounting to about 10 per cent of the material used; it crystallises in long, colourless, transparent needles, and melts at 152°. Alcoholic potash converts it into the lactone, $C_{10}H_{14}O_3$, which melts at 174°, and yields the acid $C_{10}H_{16}O_4$ on hydrolysis; the lactone is readily converted by bromine into the *bromolactone*, $C_{10}H_{13}BrO_3$, which crystallises from alcohol in lustrous silky needles, and melts at 196–197°.

Bromocamphorenic acid, $C_{10}H_{13}BrO_2$, is formed when an alcoholic solution of dibromocampholid is reduced with zinc dust and ammonia; it crystallises from alcohol in thin, lustrous, six-sided plates, and melts at 159°. The barium salt contains $2H_2O$, and the zinc, copper, and silver salts are also crystalline; the methyl salt is a fragrant oil, which boils at 255° under a pressure of 767.5 m.m. The unsaturated character of bromocamphorenic acid is indicated by its behaviour towards potassium permanganate, which is immediately decolourised by the solution in sodium carbonate, a dicarboxylic acid being produced having the formula $C_{10}H_{16}O_6$, and melting at 184°; a cold solution of bromine in chloroform is at once decolourised by the acid in the same medium, hydrogen bromide and dibromocampholid being formed.

Camphorenic acid, $C_{10}H_{16}O_4$, is obtained by reducing a boiling alkaline solution of bromocamphorenic acid with sodium amalgam; it crystallises from alcohol in colourless needles, and melts at 161°. The sodium salt crystallises from strongly alkaline solutions in silky needles; the methyl salt is a colourless oil, which boils at 215° under a pressure of 767.5 m.m., and has the odour of camphor. The anhydride, $C_{20}H_{30}O_3$, melts at 84–85°.

α -Bromocampholid, $C_{10}H_{13}BrO_2$, is obtained by the action of concentrated sulphuric acid on bromocamphorenic acid, and is isomeric with that substance; the production of an isomeric lactone under the influence of sulphuric acid, and the formation of a bromolactone on

treatment with bromine, are features which characterise β -unsaturated acids. α -Bromocampholid crystallises from alcohol in lustrous plates, and melts at 92–93°; it is indifferent towards bromine, and is hydrolysed by a boiling aqueous solution of barium hydroxide.

β -Bromocampholid is isomeric with the foregoing substance, and is formed from camphorenic acid or the sodium salt and bromine; it crystallises from ether in transparent prisms, and melts at 62°. It is indifferent towards bromine, and when the alcoholic solution is reduced with zinc dust and ammonia, camphorenic acid is formed.

Campholid, $C_{10}H_{16}O_2$, is obtained by dissolving camphorenic acid in concentrated sulphuric acid, the change being parallel with that attending the conversion of bromocamphorenic acid into α -bromocampholid; it is very readily soluble in most organic solvents, but separates from petroleum in minute white crystals, and melts at 176–177°. Campholid is very volatile, and sublimes slowly below 100°; it resembles camphor in appearance, and has the odour of that substance. It is indifferent towards bromine, but yields an acid, $C_{10}H_{18}O_3$, on hydrolysis, which crystallises from ethylic acetate in magnificent lustrous needles, melting at 179°.

*143. "Isomeric π -Bromo- α -nitro Camphors." By ARTHUR LAPWORTH, D.Sc., and F. STANLEY KIPPING, Ph.D., D.Sc.

It has already been shown by one of the authors (*Proc. Chem. Soc.*, cxlviii., 39) that π -dibromo-camphor is attacked by concentrated nitric acid, and that the product consists partly of a bromocamphoric acid and partly of an oil, which, by the action of alcoholic potash, yields a bromonitro-camphor.

It has now been found that if this oil be boiled with concentrated nitric acid until it is free from π -dibromocamphor; it subsequently solidifies to a crystalline cake, from which *bromonitro-camphor* can be easily isolated. (Found C=34.05; H=4.21; Br=44.98 per cent. Calc. C=33.80; H=3.67; Br=45.05 per cent.)

This compound separates from cold light petroleum in the form of long flat needles, melting at 54°, and is insoluble in water, but soluble in most of the usual organic solvents. When boiled with alcoholic potash it loses 1 atom of bromine, and affords the potassium salt of the bromonitro-camphor previously described (*loc. cit.*). The further investigation of this bromonitro-camphor leads to the conclusion that it is polymorphous. The crystals from chloroform and petroleum melt sharply at 133–134°, and solidify on cooling to a crystalline mass, which fuses at 126°; this is also the melting-point of crystals obtained from alcoholic or dilute acetic acid solutions, whereas large pyramidal crystals deposited from a mixture of ethylic acetate and chloroform melt at 108°, immediately solidify, and melt once more at 126°. A 6 per cent solution gave $[\alpha]_D = +33.04$.

Reduction of π -bromo- α -nitro-camphor with zinc dust and acetic yields an amido-compound with a strong ammoniacal odour, which is probably ordinary amido-camphor, as it contains no bromine, and agrees in properties with the compound described by Schiff (*Ber.*, xiii., 1404).

If, however, the bromonitro-camphor be carefully reduced with sodium amalgam in alkaline solution, it is converted into a new π -bromo- α -amido-camphor,—



the hydrochloride of which crystallises from water or acetone in colourless needles or plates. (Calculated for $C_{10}H_{14}BrONH_2 \cdot HCl$, C=42.46; H=6.03; Br+Cl=40.81. Cl=12.56. Found, C=42.57; H=6.05; Br+Cl=40.36. Cl=12.70).

The oxalate is almost insoluble in water, and melts at 201°; the platinumchloride forms silky yellow needles, melting with decomposition about 219°.

π -Bromo- α -nitro-camphor dissolves in hot hydrochloric acid, and the solution on cooling deposits crystals of a new compound, which is soluble in hot sodium carbonate solution, and separates from benzene in flat needles melt-

ing at 137°. This substance is an isomeric π -bromo- α -nitro-camphor. (Found, C=43.57; H=5.32. Calculated, C=43.47; H=5.07 per cent).

It differs from its isomeride inasmuch as it dissolves readily in hot water, crystallising from the solution in thin plates melting at 108°; it is also much less soluble in ethylic acetate and in benzene, and it yields a blue copper salt, that of its isomer being pink. Its specific rotation is also much greater, viz., $[\alpha]_D = +52.7$.

That these two π -bromo- α -nitro-camphor are structurally identical is probable from the fact that they both yield π -bromo-camphoric acid on oxidation with nitric acid; it is concluded, therefore, that the difference between these two substances is of the same nature as that subsisting between *cis*- and *trans*-modifications of cycloid derivatives.

*144. "Derivatives of π -Bromocamphoric Acid." By F. STANLEY KIPPING, Ph.D., D.Sc.

π -Bromocamphoric acid, $C_{10}H_{13}BrO_4$, prepared by oxidising π -dibromocamphor (*Proc. Chem. Soc.*, cxlviii., 33), is readily acted on by alkalis giving, according to the conditions of the experiment, a lactonic acid, $C_{10}H_{11}O_4$ (m. p. 164–165°), or π -hydroxycamphoric acid, $C_{10}H_{16}O_5$ (*Proc.*, cli., 88).

The lactonic acid is the initial, and not the final, product of the action, as was at first supposed; when heated with excess of aqueous potash it is converted into a salt of the π -hydroxy acid. The hydroxy acid, treated with acetic chloride, yields an acetyl derivative of its anhydride; this substance crystallises from ethereal petroleum in prisms melting at 89–90°, and is dimorphous, another modification melting at 86–87°. When the hydroxy acid is distilled, it yields as principal product a lactonic acid, $C_{10}H_{11}O_4$ (m. p. about 226°, isomeric with the compound referred to above, and identical with that obtained by heating π -bromo-camphoric acid with quinoline (*loc. cit.*). The lactonic acid of lower melting-point is also converted on distillation into the isomeride of higher melting-point, whereas the latter, on fusion with potash, gives the π -hydroxy acid.

π -Hydroxycamphoric acid and the lactonic acid melting at 164–165° are readily oxidised by nitric acid, giving an acid of the composition $C_{10}H_{14}O_6$ (*loc. cit.*), but the lactonic acid of higher melting point is exceedingly stable, and seems not to be attacked by boiling nitric acid; on prolonged treatment with alkaline permanganate, however, either at ordinary temperatures or at 100°, it yields, amongst other products not yet investigated, a small quantity of a derivative of dihydroxycamphoric acid, $C_{10}H_{16}O_6$, namely, a hydroxylactonecarboxylic acid of the composition $C_{10}H_{14}O_5$. This substance crystallises from hot water, in which it is readily soluble, in long, slender needles, and from a mixture of moist ether and ethylic acetate in well-defined transparent prisms melting at about 265°; these crystals lose H_2O , and become opaque when heated at 100°, so that the substance is probably a monohydroxylactonic acid of the composition $C_{10}H_{14}O_5 + H_2O$, and not a dihydroxy compound. Its identity with the acid obtained from π -dibromocamphoric anhydride (see following note), and the fact that the lactone ring in the substance (m. p. 226°) from which it is derived is very stable, lead to the conclusion that it is the π -hydroxy group which has taken part in the lactone formation.

It seems probable, from the facts already established, that the π -bromine atom in π -bromocamphoric acid is a constituent of a $-CH_2Br$ group.

145. " π -Dibromocamphoric Acid and its Derivatives." By F. STANLEY KIPPING, Ph.D., D.Sc.

The derivatives of π -bromocamphoric acid, which have been referred to in the preceding and in previous notes, are so stable that attempts to obtain from them simple oxidation products containing less than 10 atoms of carbon have so far been unsuccessful; as they also resist the action of bromine, or give with it ill-defined substances,

experiments were made with the object of brominating π -bromocamphoric acid itself, in the hope of obtaining a dibromo-derivative which, on treatment with alkalis, would yield products more easily oxidisable than those prepared from the monobromo acid.

π -Dibromocamphoric anhydride, $C_{10}H_{12}Br_2O_3$, is obtained on treating dry π -bromocamphoric acid with bromine and amorphous phosphorus under the usual conditions; it crystallises from chloroform in large transparent plates, melts at about 210° without decomposing, and is readily soluble in warm chloroform, but very sparingly in cold ether, and insoluble in cold water and cold sodium carbonate solution.

π -Dibromocamphoric acid, $C_{10}H_{14}Br_2O_4$, is deposited in small plates when the anhydride is dissolved in hot concentrated nitric and the solution evaporated on the water-bath; it melts and decomposes at 210–211°, and is readily soluble in cold ether, but insoluble, or nearly so, both in chloroform and in hot water. It dissolves in dilute sodium carbonate solution with effervescence, and on acidifying the solution after heating for a few minutes π -bromocamphanic acid (see below) is precipitated. π -Dibromocamphoric acid is stable at 100°, but when heated at its melting-point, part is re-converted into the dibromo-anhydride and part is transformed into π -bromocamphanic acid with liberation of hydrogen bromide.

π -Bromocamphanic acid, $C_{10}H_{13}BrO_4$, is formed when the dibromo-anhydride is boiled for some hours with water and a little alcohol; it separates from cold dilute alcohol in fern-like crystals which contain water, but from hot water and from a mixture of chloroform and ethyl acetate anhydrous crystals are deposited; it melts at 176–177°, and is soluble in sodium carbonate solution with effervescence.

On prolonged boiling with water, or on heating with aqueous alkalis, π -dibromocamphoric acid is converted into an acid melting at about 265°, and identical with the oxidation product described in the preceding note.

146. "*w*-Bromocamphoric Acid." By F. STANLEY KIPPING, Ph.D., D.Sc.

The fact that π -bromocamphoric acid is obtained directly on oxidising π -dibromocamphor, whereas the π -dibromocamphoric acid can be prepared from the corresponding anhydride (see preceding abstract), led the author to try and isolate the unknown bromocamphoric acid corresponding with Wreden's bromocamphoric anhydride: this was accomplished by hydrolysing the anhydride with concentrated nitric acid under suitable conditions, but the yield was comparatively small, most of the anhydride being recovered.

The bromocamphoric acid, which, it is proposed, should be distinguished from the isomeric π -acid by using the initial letter of Wreden's name (he having first prepared the anhydride), crystallises from a mixture of chloroform and ether in large transparent orthorhombic pyramids, having the composition $C_{10}H_{13}BrO_4$. (Found, C=42.9; H=5.4; theory, C=43.0, H=5.4 per cent). It dissolves freely in ether, but is almost insoluble in benzene and chloroform, and melts at 195–196°, charring slightly and effervescing; it is readily soluble in sodium carbonate solution, by which it is rapidly decomposed, yielding ordinary camphanic acid. When heated for a short time with acetic chloride the acid is re-converted into the anhydride from which it is derived.

Aschan (*Ber.*, xxvii., 2112, and xxviii.; *Ref.* 922) has recently isolated an acid, which he designates *l*-bromiocamphoric acid; this compound appears to be different from the acid which forms the subject of the present communication, but Aschan's original paper being at present inaccessible, this point cannot be finally settled.

The author also refers to a curious phenomenon observed in crystallising *w*-bromocamphoric anhydride from chloroform; in some cases the solution becomes highly supersaturated, and crystallisation ultimately takes place with almost explosive violence.

147. " *π -Chlorocamphoric Acid.*" By F. STANLEY KIPPING, Ph.D., D.Sc., and WILLIAM J. POPE.

Optically inactive camphor sulphonic chloride (Kipping and Pope, *Trans.*, 1893, lxiii., 548) yields, on distillation, two products, namely, a crystalline inactive π -chlorocamphor and an oil (*Trans.*, 1895, lxvii., 371).

When the mixture of these two compounds is heated with nitric acid the oil is rapidly oxidised and passes into solution, but π -chlorocamphor, like π -dibromocamphor, is attacked and dissolved rather slowly.

On cooling the solution, crystals and an oil are deposited. The crystalline substance is π -chlorocamphoric acid, the oil being probably π -chloro- α -nitrocumphenor, the formation of which, under the above conditions, would be analogous to that of α -dibromo- α -nitrocumphenor from α -dibromocumphenor (see preceding note by Lapworth and Kipping); other substances are present in the filtrate from nitric acid, but they have not yet been examined.

Inactive π chlorocamphoric acid, $C_{10}H_{13}ClO_4$, resembles π -bromocamphoric acid very closely in ordinary properties. It is very sparingly soluble in hot water, from which it crystallises in small lustrous prisms, melting at about 195° . It is almost insoluble in chloroform, but dissolves freely in ether, methyl alcohol, and acetone.

This chloro-acid is doubtless structurally similar to π -bromocamphoric acid, but whereas the latter is a derivative of an optically active π -bromocumphenor, the chloro-acid is derived from an inactive or racemic halogen derivative of camphenor.

A chlorocamphoric anhydride has been recently described by Aschan (*Ber.*, xxviii., Ref. 922), but this substance is derived from an acid structurally as well as optically different from π -chlorocamphoric acid.

(To be continued).

NOTICES OF BOOKS.

Modern Copper Smelting. By EDWARD DYER PETERS, Jun. Seventh Edition, Re-written and greatly Enlarged. London and New York: The Scientific Publishing Company. 1895. 8vo., pp. 642.

WHEN a work of this character has passed through the ordeal of seven editions, we may feel sure that it has given satisfaction to practical men.

The present edition takes due account of certain capital improvements in the metallurgy of copper, such as the introduction of automatic calcining furnace, the rapid development of the copper Bessemer process, the improvements in blast-furnaces and reverberatories, and "perhaps, above all, by the gradual dawning of the idea that although copper is worth fifteen times as much as iron it is not absolutely necessary to expend fifteen times as much money in handling and treating its ores."

This is a specimen of the dry humour which crops out here and there in this work. Thus we read that "it is easier to run a furnace on a novel plan with men who know nothing about it than with those who know too much."

On again speaking of cliques among workmen, Mr. Peters writes:—"A judicious mixture of nationalities will often prevent the deceptions and the attitude of passive resistance to all improvements which characterise a body of experienced workmen of any one nationality. A mixture of Irish and Cornish furnace-men with an American foreman usually works well, as the men all dislike and distrust each other so much that they find it impossible to combine against the common enemy."

The chapter on the distribution of the ores of copper loses much in value by its being confined to the North American deposits.

Automatic sampling is an improvement which must do away with some very unedifying disputes and recrimina-

tions, not merely in metallurgy, but in all the "heavy" chemical industries.

The Cornish fire assay of copper ores—a "*Pierde-methoda*" as we have heard it called in Germany—is spoken of with too great leniency. A process which gives results short of the truth, not by a constant value, but by a proportion which fluctuates in different ores, ought no longer to be recognised. It is an error to say, as the author does in a foot-note, that "in England all analytical chemists are called assayers," though the exact connotation of the two terms has never been authoritatively defined. The electrolytic process for the determination of copper is very fully described and illustrated.

Under the cyanide assay, attention is called to the substances which interfere with the result. Arsenic and antimony rank as the most dangerous substances, as also zinc in proportions exceeding 4½ per cent. Ferric hydroxide, if present in quantity, occludes copper and introduces a serious error. Yet we once met with a chemist who considered he had effected an improvement in this process by omitting to filter off the precipitate of ferric hydroxide before titrating with cyanide.

In the improved cyanide method of A. H. Law, the copper is first precipitated from the solution of the ore by means of metallic aluminium, the deposit is re-dissolved by means of nitric acid. Silver, if any, is precipitated as a chloride and filtered off. For the subsequent titration care is taken that all the conditions shall be identical, such as the total volume of the solution, the proportion of ammonia used, and the working temperature.

The iodide process is very highly spoken of. After giving a table of results, the question is put—"Can the electrolytic method improve upon this?"

Pyritic smelting, in the strict sense of the term, i.e., without the use of any carbonaceous fuel, is not, the author considers, sufficiently developed to warrant its introduction, except experimentally.

The Bessemer treatment of copper forms the subject of a very interesting chapter.

The most harmful substance which may be present in a matte is bismuth, as it adheres to copper most obstinately; and, according to the experiments of Hampe, renders it red-short even when occurring in such small proportions as 0.02 per cent.

The electrolytic refining of copper seems to have proved very successful in America, as shown by the enlargement of existing electrolytic works, and the establishment of new ones on the same principle.

A most valuable feature of the work must be recognised in the numerous and elaborate illustrations.

It is scarcely needful to add that the present edition of this book must be welcomed as a boon by all persons connected with the copper industry.

Treatise on Distillery. Distillers' Microbiology. Ferments and Fermentation. ("Traité de Distillerie. Microbiologie du Distillateur. Ferments et Fermentation"). By M. P. GUICHARD, Member of the Chemical Society of Paris. Paris: J. B. Baillière et Fils. 1896. Pp. 392, 16mo.

THE study of fermentation is not merely a technological question. It was the earliest subject which led us to a clear conviction that chemical phenomena may involve and depend upon biological processes. This fact is of profound scientific importance. It shows us that the simpler sciences of Comte's hierarchy may and do require a knowledge of those more complex and less general.

But the work before us does more than it promises. It considers the animal and vegetable proteic matters, the soluble and figured ferments, and the industrial analysis of fermented products.

The author gives a historic study of the process of fermentation. He traces the discovery of alcohol to Abucasi and Arnold, of Villanova, and quotes a recipe from

Ramon Lully for its production. He briefly traces the gradual development of the theory of fermentation and putrefaction down from those early experimentalists to the full light thrown upon the subject by Pasteur.

In the second part, M. Guichard considers the albumenoid substances in the widest sense of the word, the albumens, globulines, peptones, collagens, caseins, together with the genesis and transformation of the albumenoids in the organic economy.

The third section is devoted to the soluble ferments, diastases, zymoses or enzymes, and the theory of their action.

In the fourth section, we pass to the figured ferments—moulds, their aerobic and anaerobic life; yeasts, their origin, purification, and chemical composition. There is also an account of the reagents and pigments used in their microscopic examination. The microscope here figured and recommended is that of Véric. For photographing the ferments we find the instruments of Dr. Roux (manufactured by Véric) and of Nachet recommended and shown in the illustrations. As useful reagents, the author recommends a hot solution of glycerin, diluted sodium sulphate, and alum in very dilute solution, potassium acetate in an aqueous solution, the reagents of Barfoed, Fehling, Millon, and Ehrlich. The last-mentioned consists of 2 parts of potassium dichromate and 0.50 part copper sulphate in 100 parts water. The stains or dyes found most useful are described at some length.

In the fifth section we have the classification of fermentations, as the alcoholic, the bacterial (under which head are given some interesting facts as concerning the vital conditions of the Schizomycetes and the low temperatures which they are able to support), the acetic, the lactic, butyric, panary, gluconic, and mannitic.

The sixth section is occupied with the industrial analysis of the products of fermentation.

A selection of useful tables conclude the work.

M. Guichard's book may be regarded as useful, both from a practical and a theoretical point of view. Few chemists can now afford to overlook the multiform and far-reaching agency of fermentation.

CORRESPONDENCE.

ON THE

PLACE OF HELIUM IN THE CLASSIFICATION OF ELEMENTARY SUBSTANCES.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS, vol. lxxii., p. 305, I notice that Dr. Gladstone maintains his wrong assertion "that the successive differences between the atomic weights of adjacent members of the metals in the first group in Mendeleeff's table showed that these differences increased as we go downwards," notwithstanding that the assertion was disproved by reference to this table, as well as to the one set forth in my former letter.

Judging from the remarkable statements now made by Dr. Gladstone, it would appear to be much more probable that he has forgotten the numbers he wrote on the blackboard of the Physical Society than that the official record of these numbers is incorrect.

As Dr. Gladstone, at the meeting of this Society, expressed doubt as to the elementary character of helium, he is hardly entitled to have an opinion on its place in any classification until he has first convinced himself on this point.

His observations on the relations of the atomic weights in the year 1853 have little in common with those set forth in my tables in the CHEMICAL NEWS of 1878 (vol. xxxviii.), which, as will be seen, anticipated everything of value that Dr. Gladstone advanced respecting the atomic

weights in his Address to the Chemical Section of the British Association in 1883. No chemist knows this better than Dr. Gladstone himself.—I am, &c.,

H. WILDE.

December 21, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Seances, de l'Academie des Sciences. Vol. cxxi., No. 23, December 2, 1895.

Presence of Sodium in Aluminium produced by Electrolysis.—Henri Moissan.—This memoir will be inserted in full.

Origin of Argon and of Helium in the Gases given off by certain Sulphurous Springs.—L. Troost and L. Ouvard.—(See p. 309).

Studies in Molecular Physics.—Ch. V. Zenger.—The author announces that he has found a simple relation between the density and the specific heat of the elements. This relation seems to him to throw a new light on the molecular actions which have governed the formation of the elements. Perhaps by imitating the characteristic conditions of the most remote geological epochs we may succeed in transforming the physical and chemical properties of the elements themselves.

Relation between the Intensity of Light and the Chemical Decomposition which it produces. Experiment with Mixtures of Ferric Chloride and Oxalic Acid.—Georges Lemoine.—The decomposition occasioned by light in solutions of ferric chloride and oxalic acid may serve for measuring the intensity of the light although the reaction is exothermic, for the heat disengaged is rapidly dissipated in the ambient medium, and the chemical transformation takes a permanent course. We may conclude approximately that the chemical decomposition of the mixture of ferric chloride and oxalic acid is proportional to the luminous intensity.

Presence of Argon and Helium in a Source of Natural Nitrogen.—Ch. Moureu.—(See p. 310).

Experimental Determination of the Agglutinating Power of Coal.—Louis Campredon.—There is no correlation between the composition of a coal as established by analysis and its caking power.

On Chromium Amalgam and on some Properties of Metallic Chromium.—J. Féré.—The author obtains chromium-amalgam by the electrolytic method. The product obtained had the composition Hg_3Cr . On submitting this compound to a pressure of 200 kilos. per square centimetre between folds of filter-paper another amalgam was obtained of the constant composition of $HgCr$.

Synthesis of Complex Amides.—Albert Colson.—Not suitable for useful abridgment.

New Instances of Superposition of the Optical Effects of Asymmetric Carbons.—Ph. A. Guye and Ch. Goudret.—Not suitable for abridgment and not of sufficient importance for insertion *in extenso*.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xxxi., No. 2.

Desulphuration of Cast Metal by the Saniter Process.—Krewtsoff.—The ingredient used is chiefly calcium chloride. In samples obtained the proportion of sulphur before the addition of the calcium chloride was from 0.029 to 0.035. After the process it was reduced to 0.019 to 0.016.

Determination of Sulphur in Organic Substances.
L. L. de Koninck and Ed. Nihoul.—The authors submit the specimen operated upon to combustion with a mixture which they call nitro-lime. At least 5 parts of quicklime are incorporated with 1 part of dry calcium nitrate. The 5 parts of quicklime, in minute fragments quite anhydrous and free from sulphate and silicate, are placed in a porcelain capsule and gradually sprinkled with 1 part of dry calcium nitrate dissolved in $\frac{1}{4}$ part water, applying a moderate heat if needful to set the reaction in progress. The method of operation has a general resemblance to that used in the Varrentrap and Will process for determining nitrogen.

MISCELLANEOUS.

The East London Exhibition.—It is announced that in June next there will be held, in the People's Palace, a General Exhibition of the Trades, Industries, and Arts of East London, and of the work of the Polytechnics and Technical Institutes. It includes the following Sections:—Exhibits of manufacturing and trading firms, the work of individual craftsmen; exhibits by individual students and apprentices; exhibits by students, collectively and by institutions; women's work, and loan exhibits of works of art. The first Section comprises the following groups:—The building trades; the silver trades, goldsmiths, jewellers, &c.; printing and allied trades; leather trades; clothing trades; engineering and metal trades; food and cookery; furnishing and brush and basket trades; shipping and navigation; tobacco trades; glass and pottery trades; coach-makers, wheelwrights, and auxiliary trades; textile trades; horticulture; aeronautics; brewing, and manufacture of aerated waters; fuel furnaces, stoves, and fireplaces; india rubber; photography; educational and physical training appliances; toys and games; bicycles and tricycles; coopers; musical instruments; chemical manufactures—a department in which we have still much to learn; fire-arms and explosives; and, lastly, taxidermy. This last item will, we fear, include much that is injurious, if not absolutely criminal, *i. e.*, the destruction of harmless and useful birds and insects at the bidding of fashion. Under Section II. we find scientific instrument making, a department in which we have, nationally speaking, no little room for improvement. Prizes will be awarded in the various groups for excellence of workmanship. We hope that the Exhibition may prove successful in every sense, and that it may revive the original object of the People's Palace.

MEETINGS FOR THE WEEK.

TUESDAY, Dec. 31st. } Royal Institution, 3. (The Christmas Lec-
THURSDAY, Jan. 2nd. } tures). "Sound, Hearing, and Speech."
SATURDAY, Jan. 4th. } by Prof. J. G. McKendrick, M.D., F.R.S.
FRIDAY, 3rd. — Quekett Club, 8.
— Geologists' Association, 8.

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